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ANNUAL REPORTS

ON THE

PROGRESS OF CHEMISTRY.

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ANNUAL REPORTS

ON THE

PROGRESS OF CHEMISTRY

FOR 1905.

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TABLE OF ABBREVIATIONS EMPLOYED IN THE REFERENCES.

Abbreviated Title.	Journal.
Amer. Chem. J.	American Chemical Journal.
Amer. Geol.	American Geologist.
Amer. J. Pharm.	American Journal of Pharmacy.
Amer. J. Physiol.	American Journal of Physiology.
Amer. J. Sci.	American Journal of Science.
Analyst	The Analyst.
Annalen	Justus Liebig's Annalen der Chemie.
Ann. Physik	Annalen der Physik.
Ann. agron.	Annales agronomiques.
Ann. Chim. anal.	Annales de Chimie analytique appliquée à l'Industrie, à l'Agriculture, à la Pharmacie et à la Biologie.
Ann. Chim. Phys.	Annales de Chimie et de Physique.
Ann. Inst. Pasteur	Annales de l'Institut Pasteur.
Ann. sci. Univ. Jassy	Annales scientifiques de l'Université de Jassy.
Arbb. Kais. Ges.	Arbeiten aus dem Kaiserlichen Gesundheitsamt.
Arch. Exp. Path. Pharm.	Archiv für experimentelle Pathologie und Pharmakologie.
Arch. Hygiene	Archiv für Hygiene.
Arch. Néerland.	Archives Néerlandaises des sciences exactes et naturelles.
Arch. Pharm.	Archiv der Pharmazie.
Arch. Sci. biol. St. Petersburg	Archives des Sciences biologiques, St. Petersbourg.
Arch. Sci. phys. nat.	Archives des Sciences physiques et naturelles.
Atti R. Accad. Sci. Torino	Atti della Reale Accademia delle Scienze di Torino.
Atti R. Accad. Lincei	Atti della Reale Accademia dei Lincei.
Beitr. chem. Physiol. Path.	Beiträge für chemische Physiologie und Pathologie.
Ber.	Berichte der Deutschen chemischen Gesellschaft.
Ber. Deut. pharm. Ges.	Berichte der Deutschen pharmazeutischen Gesellschaft (Berlin).
Berlin Klin. Woch.	Berliner Klinische Wochenschrift.
Bied. Centr.	Biedermann's Centralblatt für Agrikulturchemie und rationellen Landwirtschafts-Betrieb.
Bihang K. Svenska Vet.-Akad. Handl.	Bihang till Kongl. Svenska Vetenskaps-Akademiens Handlingar.
Brit. Med. J.	British Medical Journal.
Bull. Acad. roy. Belg.	Académie royale de Belgique—Bulletin de la Classe des Sciences.
Bull. Acad. Sci. Cracow	Bulletin international de l'Académie des Sciences de Cracovie.
Bull. Assoc. Chim. Sucr. Dist.	Bulletin de l'Association des Chimistes de Sucrérie et de Distillerie.
Bull. Coll. Agr. Tōkyō	Bulletin of the College of Agriculture, Imperial University, Tōkyō.
Bull. Geol. Soc. Amer.	Bulletin of the Geological Society of America.

Abbreviated Title.	Journal.
Bull. Soc. Chim.	Bulletin de la Société chimique de Paris.
Bull. Soc. franç. Min.	Bulletin de la Société française de Minéralogie.
Bull. Soc. ind. Mulhouse	Bulletin de la Société industrielle de Mulhouse.
Centr. Bakt. Par.	Centralblatt für Bakteriologie, Parasitenkunde und Infektionskrankheiten.
Centr. Min.	Centralblatt für Mineralogie, Geologie und Palaeontologie.
Chem. Centr.	Chemisches Centralblatt.
Chem. News	Chemical News.
Chem. Rev. Fett Harz Ind.	Chemische Revue über die Fett- und Harz-Industrie.
Chem. Zeit.	Chemiker Zeitung.
Compt. rend.	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.
Compt. rend. Soc. Biol.	Comptes rendus des Séances de la Société de Biologie.
Exper. Stat. Record	Experiment Station Record.
Farm. Tid.	Farmaceutisk Tidsskrift.
Föld. Közlöny	Földtani Közlöny.
Gazzetta	Gazzetta chimica italiana.
Geol. Mag.	Geological Magazine.
Jahrb. Min.	Neues Jahrbuch für Mineralogie, Geologie und Palaeontologie.
Jahrb. Min. Beil.-Bd.	Neues Jahrbuch für Mineralogie, Geologie und Palaeontologie. Beilage-Band.
Jahrb. Radioakt. Elek.	Jahrbuch für Radioaktivität und Elektronik.
J. Agric. Sci.	Journal of Agricultural Science.
J. Amer. Chem. Soc.	Journal of the American Chemical Society.
J. Amer. Med. Assoc.	Journal of the American Medical Association.
J. Chem. Metall. Mining Soc. South Africa	Journal of the Chemical, Metallurgical, and Mining Society of S. Africa.
J. Chim. phys.	Journal de Chimie physique.
J. Fed. Inst. Brewing.	Journal of the Federated Institutes of Brewing.
J. Geol.	Journal of Geology.
J. Hygiene	Journal of Hygiene.
J. Landw.	Journal für Landwirtschaft.
J. Med. Research	Journal of Medical Research.
J. Path. Bact.	Journal of Pathology and Bacteriology.
J. Pharm. Chim.	Journal de Pharmacie et de Chimie.
J. Physical Chem.	Journal of Physical Chemistry.
J. Physiol.	Journal of Physiology.
J. Physique	Journal de Physique.
J. pr. Chem.	Journal für praktische Chemie.
J. Roy. Agric. Soc.	Journal of the Royal Agricultural Society.
J. Roy. Soc. New South Wales	Journal of the Royal Society of New South Wales.
J. Russ. Phys. Chem. Soc.	Journal of the Physical and Chemical Society of Russia.
J. Soc. Chem. Ind.	Journal of the Society of Chemical Industry.
Landw. Versuchs-Stat.	Die landwirtschaftlichen Versuchs-Stationen.
L'Orosi	L'Orosi.
Mem. Accad. Sci. Torino	Memorie della Reale Accademia delle Scienze di Torino.
Mem. Manchester Phil. Soc.	Memoirs and Proceedings of the Manchester Literary and Philosophical Society.
Mem. R. Accad. Lincei	Memoires della Reale Accademia dei Lincei.
Milch Zeit.	Milch Zeitung.
Milchw. Zentr.	Milchwirtschaftliches Zentralblatt.
Min. Mag.	Mineralogical Magazine and Journal of the Mineralogical Society.
Monatsh.	Monatshefte für Chemie und verwandte Theile anderer Wissenschaften.
Mon. Sci.	Moniteur Scientifique.
Nuovo Cim.	Il Nuovo Cimento.

Abbreviated Title.	Journal.
Öfver K. Vet.-Akad. Förh.	Öfversigt af Kongl. Vetenskaps-Akademiens Förhandlingar.
Pflüger's Archiv.	Archiv für die gesammte Physiologie des Menschen und der Thiere.
Pharm. Arch.	Pharmaceutical Archives.
Pharm. Centr. H.	Pharmazeutische Centralhalle.
Pharm. J.	Pharmaceutical Journal.
Pharm. Rev.	Pharmaceutical Review.
Pharm. Weekblad	Pharmaceutisch Weekblad.
Pharm. Zeit.	Pharmazeutische Zeitung (Berlin).
Phil. Mag.	Philosophical Magazine (The London, Edinburgh and Dublin).
Phil. Trans.	Philosophical Transactions of the Royal Society of London.
Phys. Proc.	Proceedings of the Physical Society.
Phys. Zeit.	Physikalische Zeitschrift.
Proc.	Proceedings of the Chemical Society.
Proc. Amer. Physiol. Soc.	Proceedings of the American Physiological Society.
Proc. Camb. Phil. Soc.	Proceedings of the Cambridge Philosophical Society.
Proc. Phil. Soc. Glasgow	Proceedings of the Glasgow Philosophical Society.
Proc. Physiol. Soc.	Proceedings of the Physiological Society.
Proc. K. Akad. Wetensch. Amsterdam.	Koninklijke Akademie van Wetenschappen te Amsterdam. Proceedings (English Version).
Proc. Roy. Soc.	Proceedings of the Royal Society.
Proc. Roy. Soc. Edin.	Proceedings of the Royal Society of Edinburgh.
Proc. Washington Acad. Sci.	Proceedings of the Washington Academy of Science.
Quart. J. Geol. Soc.	Quarterly Journal of the Geological Society.
Rev. intern. Falsif.	Revue internationale des Falsifications.
Rec. trav. chim.	Receuil des travaux chimiques des Pays-Bas et de la Belgique.
Rev. Metallurgie	Revue de Metallurgie.
Revista Min.	Revista Minera.
Sci. Proc. Roy. Dubl Soc.	Scientific Proceedings of the Royal Dublin Society.
Sci. Trans. Roy. Dubl. Soc.	Scientific Transactions of the Royal Dublin Society.
Sitzungsber. K. Akad. Wiss. Berlin.	Sitzungsberichte der Königlich Preussischen Akademie der Wissenschaften zu Berlin.
Sitzungsber. K. Akad. München.	Sitzungsberichte der königlich bayerischen Akademie der Wissenschaften in München.
Skand. Arch. Physiol.	Skandinavisches Archiv für Physiologie.
Trans.	Transactions of the Chemical Society.
Trans. Amer. Inst. Mining Eng.	Transactions of the American Institute of Mining Engineers.
Trans. Faraday Soc.	Transactions of the Faraday Society.
Trans. Nova Scotia Inst. Sci.	Transactions of the Nova Scotia Institute of Science.
Trans. Path. Soc. Lond.	Transactions of the Pathological Society, London.
Trans. Roy. Dubl. Soc.	Transactions of the Royal Dublin Society.
Trans. Roy. Irish Acad.	Transactions of the Royal Irish Academy.
Trans. Roy. Soc. Canada	Transactions of the Royal Society of Canada.
Trans. Roy. Soc. S. Australia	Transactions of the Royal Society of S. Australia.
Tsch. Min. Mitth.	Tschermak's Mineralogische Mittheilungen.
U.S.A. Dept. Agric. Bull.	Bulletins of the Department of Agriculture, U.S.A.
U.S.A. Dept. Agric. Rep.	Reports of the Department of Agriculture, U.S.A.
Wien. Sitzungsber.	Sitzungsberichte der Kaiserlich Akademie der Wissenschaften zu Wien.
Wiss. Abhandl. Phys.-Tech. Reichsanstalt.	Wissenschaftliche Abhandlungen der Physikalisch-Technischen Reichsanstalt.
Woch. Brau.	Wochenschrift für Brauerei.
Zeit anal. Chem.	Zeitschrift für analytische Chemie.
Zeit. angew. Chem.	Zeitschrift für angewandte Chemie.
Zeit. anorg. Chem.	Zeitschrift für anorganische Chemie.

Abbreviated Title.	Journal.
Zeit. Biol.	Zeitschrift für Biologie.
Zeit. Elektrochem.	Zeitschrift für Elektrochemie.
Zeit. Farb. Text. Ind.	Zeitschrift für Farben- und Textil-Industrie.
Zeit. Kryst. Min.	Zeitschrift für Krystallographie und Mineralogie.
Zeit. land. Versuch. wes. Ost.	Zeitschrift für das landwirtschaftliche Versuchswesen in Österreich.
Zeit. Nahr. Genussm.	Zeitschrift für Untersuchung der Nahrungs- und Genussmittel.
Zeit. öffentl. Chem.	Zeitschrift für öffentliche Chemie.
Zeit. physikal. Chem.	Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre.
Zeit. physiol. Chem.	Hoppe-Seyler's Zeitschrift für physiologische Chemie.
Zeit. prakt. Geol.	Zeitschrift für praktische Geologie.
Zeit. Ver. deut. Zuckerind.	Zeitschrift des Vereins der deutschen Zucker-Industrie.
Zeit. Zuckerind. Böhm.	Zeitschrift für Zuckerindustrie in Böhmen.

ANNUAL REPORTS

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GENERAL AND PHYSICAL CHEMISTRY.

The work on physical chemistry published during the year has been for the most part on lines already well defined, and little of essential novelty has to be chronicled.

In the domain of solutions, great activity has been displayed, the nature of colloidal solutions in particular being the subject of much research and abundant speculation. The most important experimental contribution to our knowledge of aqueous solutions is undoubtedly the work of Morse and Frazer on the osmotic pressure of solutions of cane sugar. These investigators have succeeded in repeating and amplifying Pfeffer's experiments, and the results of their further investigations may be awaited with interest.

The year has not passed without its due quota of hypotheses, mutually destructive for the most part, to account for the non-obedience of strong electrolytes to Ostwald's dilution law. This remains the most formidable problem of the electrolytic dissociation theory, and a general solution seems as remote as ever.

The study of the mechanism of the action of ferments has led to a similar profusion of hypotheses of the most varied type. Experimental investigation of this subject is, however, being briskly carried on, and may in the course of a few years lead to a definite theory.

Atomic Weights.

R. Luther suggests[1] that the unit of atomic weights might be connected with the C.G.S. system through Faraday's Law. For example, one might take as unit of atomic weight that quantity of a monad element in grams which carries a charge of 10^4 C.G.S. electromagnetic

[1] *Zeit. Elektrochem.*, 1905, **11** 273.

units. This would involve raising the present atomic weights by about 3·5 per cent.

A system for calculating mean values of atomic weights from observations is given by Julius Meyer.[1] If a is the desired gravimetric ratio $M : U$, then actual experiments will yield

$$a_1 = M_1 : U_1, \quad a_2 = M_2 : U_2, \quad a_3 = M_3 : U_3, \text{ &c.},$$

and the problem is to find from the separate values the most probable value of a. Assuming that the "weight" of each observation is proportional to the quantity of substance taken,

$$a = \frac{a_1 M_1 + a_2 M_2 + a_3 M_3 + \ldots}{M_1 + M_2 + M_3 + \ldots},$$

or since $a_1 = \frac{M_1}{U_1}$, &c.,

$$a = \frac{\Sigma \frac{M^2}{U}}{\Sigma M}.$$

The author shows in detail the application of his method to the calculation of the atomic weight of sulphur, and compares his results with those obtained by the methods of computation of Ostwald and of Clarke. The author claims that his method applied to different sets of experiments gives smaller differences from the general mean.

The minimum concentration at which an alkaline solution of fluorescein or eosin will exhibit fluorescence has been investigated by W. Spring.[2] To the naked eye, the fluorescence disappears at a concentration of 10^{-8} grams per c.c. When the solution is illuminated by a brilliant electric ray from spark and reflector, the fluorescence is still visible at a concentration of 10^{-13} grams per c.c. This would correspond to a maximum weight of the hydrogen atom of $2{\cdot}5 \times 10^{-21}$ grams. The value according to the kinetic theory is of the order 10^{-25}, so that the experiment is so far in agreement with the theoretical value.

J. H. Poynting and P. Phillips[3] have made accurate experiments to ascertain whether a substance exhibits any variation in weight with change of temperature. They conclude that the temperature-coefficient of weight cannot have a value exceeding 10^{-10} per degree centigrade.

Normal Gaseous Molecular Weights.

D. Berthelot[4] arrived at the exact molecular weights of gases by the method of limiting densities, and established the value 22·412 litres as

[1] *Zeit. anorg. Chem.*, 1905, **43**, 242.
[2] *Bull. Acad. Roy. Belg.*, 1905, 201.
[3] *Proc. Roy. Soc.*, 1905, **76** *A*, 445.
[4] *Ann. Reports*, 1904, 3.

the theoretical gram-molecular volume. P. A. Guye[1] utilises this result in connection with general formulæ for determining the exact molecular weights of gases from the normal litre weight and the values of a and b in van der Waals' equation as derived from the critical data. Guye and Friderich have already shown that the constants a and b of the equation of state referred to unit volume,

$$\left(p+\frac{a}{v^2}\right)(v-b)=(1+a)(1-b)(1+at),$$

must theoretically satisfy the following relation,

$$\frac{M}{L}(1+a)(1-b)=\text{gram-mol. vol.}=22{\cdot}412 \text{ litres},$$

M being the molecular weight of the gas referred to O = 32, and L being the weight of the normal litre (that is, at 0°, and 1 atmosphere at the sea-level under 45° latitude). The difficulty in applying this formula to the exact calculation of M lies in the fact that a and b are not in reality constant, and that their values deduced from the critical data cannot therefore be introduced directly into the above equation.

From a consideration of the p-v data for gases, the author gives two modifications of the formula which permit the use of a and b as determined from the critical magnitudes.

I. For gases permanent at 0° the following relation may be used:

$$M=\frac{(22{\cdot}412+mT_cL)}{(1+a)(1-b)}.$$

The coefficient $m=0{\cdot}0000623$ is fixed from the data for oxygen; T_c is the critical temperature on the absolute scale.

II. For gases liquefiable at 0°, the relation takes the form

$$M=\frac{22{\cdot}412L}{(1+a_o)(1-b_o)},$$

in which

$$a_o=a\left(\frac{T_c}{T}\right)^{\frac{3}{2}} \text{ and } b_o=b\left(1+\frac{T_c-T}{T_c}\right)\left(1-0{\cdot}0032229\frac{p_c}{p}\right).$$

Applying these formulæ, the author finds the following molecular weights:

	O_2.	H_2.	N_2.	CO.	Ar.
I.	32	2·0153	28·013	28·003	39·866

	CO_2.	N_2O.	SO_2.	HCl.	C_2H_2.
II.	44·003	44·000	64·065	36·484	26·018

[1] *J. Chim. Phys.*, 1905, **3**, 321.

From these molecular weights, the following atomic weights may be deduced :

Hydrogen.	Carbon.	Nitrogen.	Chlorine.
1·0077 from H_2	12·001 from CO	14·007 from N_2	35·476 from HCl
	12·003 ,, CO_2	14·006 ,, N_2O	
	12·002 ,, C_2H_2		

Sulphur.	Argon.
32·065 from SO_2	39·866 from A

These values agree well with those calculated by D. Berthelot and with the best gravimetric determinations.

Molecular Weight Determination.

E. Grimsehl[1] describes an apparatus for determining by means of a sensitive manometer the weight of a column of vapour relatively to that of air at the same temperature and pressure. The calculation of the density takes the simple form

$$s = C_1 + C_2 p,$$

where p is the difference in the manometric readings for air and vapour, and C_1 and C_2 are constants which are determined once for all. The manometer may be graduated so as to give vapour densities or molecular weights directly. The advantage of the method is that no weighing or measurement of volume is requisite, and the author claims that a molecular weight determination may be made with his apparatus in two minutes.

An apparatus for use with solvents of high boiling point is described by L. Rügheimer,[2] and the method is applied to the determination of the molecular weights of certain salts by Rügheimer in conjunction with E. Rudolfi.[3] Instead of calculating molecular weights by means of a constant from the elevation of boiling point directly, the authors calculate from it, by means of the boiling-point curve (of which only a small portion in the region of experiment need be ascertained from two observations of the boiling points of the solvent at neighbouring pressures), the relative lowering of the vapour pressure, and from this the molecular weight. The use of a constant is thus avoided, and the method is specially useful when measurements are made under different pressures, or when the high boiling point of the solvent precludes the use of a mercury thermometer. Since the thermometric observations merely serve to determine pressures, the graduation of the thermometer may be arbitrary. In the apparatus as described, an air thermometer is employed.

[1] *Zeit. angew. Chem.*, 1905, **18**, 734.

[2] *Annalen*, 1905, **339**, 297. [3] *Ibid.*, 311, 349.

Bismuth chloride (b. p. 447°) was found to be a suitable solvent for metallic chlorides, a great many of which were investigated. The results show that in no case is more than one atom of metal contained in the molecule of the chloride when dissolved in this solvent, the molecular weights agreeing with the simplest empirical formula. The higher molecular weights found for chlorides in the vaporous state are attributed to molecular association. Bismuth phosphate gives values between 261 and 326, the molecular weight corresponding to the formula $BiPO_4$ being 303.

Boiling Points in Homologous Series.

S. Young[1] has pointed out an interesting regularity in the boiling points of members of homologous series. It is that the rise of boiling point for an increment of CH_2 is mainly a function of the absolute temperature, and may be expressed with considerable accuracy by the formula

$$\Delta = \frac{144{\cdot}86}{T^{0{\cdot}0148\sqrt{T}}}.$$

Here Δ expresses the difference between the substance of boiling point T in the absolute scale and its next higher homologue. In the series of normal saturated hydrocarbons from CH_4 to $C_{19}H_{40}$, the maximum divergence between the calculated and observed boiling points is 2·3°. When other series are considered, the first two or three members are generally abnormal, in conformity with the experience gained in the application of all other formulæ to such series. Neglecting these lower members of the series, the results of the author's comparison between experimental and calculated numbers may be seen in the following table:

	No. of values of Δ.	Mean value of the difference (calc. − obs.).
Non-associating substances	49	−0·05
Esters	67	+1·53
Associating substances	28	+3·40

Osmotic Pressure.

A. Battelli and A. Stefanini[2] discuss the nature of osmotic pressure. They adopt as the most satisfactory theory a modification of Traube's view[3] that the phenomena of osmosis are due to a difference of surface tension. The direction of the osmosis is determined by this difference, and is always such that the difference between the surface tensions of the

[1] *Phil. Mag.*, 1905, [vi], **9**, 1.
[2] *Atti R. Accad. Sci. Lincei*, 1905, [v], **14**, ii, 3.
[3] *Phil. Mag.*, 1904, [vi], **8**, 704.

two liquids ultimately vanishes, a condition which does not necessarily imply that the osmosis takes place exclusively from the liquid with smaller to that with greater surface tension. If the membrane is impermeable to one of the components, the movement of the other alone can reduce the difference ; if both liquids (say alcohol and water) can pass through the membrane, the direction is chiefly that which brings about the more rapid reduction of the difference of surface tension. If a semi-permeable membrane separates two solutions which are not isotonic, but which have the same surface tension, there will be no difference of pressure on the two sides of the membrane. The authors adduce experiments by Oker Blom[1] in support of this contention. Truly semi-permeable membranes in the thermodynamic sense do not, in their opinion, exist.

S. U. Pickering[2] described an experiment which seemed to show that when a porous pot containing a 57 per cent. solution of propyl alcohol was immersed either in pure water or in pure propyl alcohol the pure liquid in each case passed into the solution. This behaviour Pickering ascribed to the permeability of the pot for either of the pure liquids and its impermeability for the hydrate formed by their union in the solution. The experiment has been repeated by A. Findlay and F. C. Short[3] and by P. S. Barlow,[4] who agree in finding that the difference in pressure observed by Pickering is not an equilibrium difference but merely temporary. When the porous pot is furnished with a copper ferrocyanide membrane, the pressure rises when the pot is immersed in water, and falls when it is immersed in propyl alcohol. Pickering's experiment therefore does not justify his conclusion.

An important series of measurements of the osmotic pressure of solutions of cane sugar has been made by H. N. Morse and J. C. W. Frazer.[5] Great care was taken in the selection of porous cells and the deposition of continuous copper ferrocyanide membranes within them, according to the process previously published by the authors.[6] After testing nearly 500 cells made at various potteries, the authors did not find one suitable for exact osmotic measurements, but eventually they succeeded in making in the laboratory several cells possessing the required properties. The formation of the membranes within these cells and the mode of connecting the manometer are described in great detail. After many experiments had been made, it became apparent that the authors had not devoted sufficient attention to maintaining the temperature absolutely constant while osmotic equilibrium was being reached. Even comparatively slight fluctuations of temperature may, if rapid, lead to considerable error in the measurements of osmotic

[1] *Zeit. physikal. Chem.*, 1901, **31**, 744.
[2] *Ber.*, 1891, **24**, 3639.
[3] *Trans.*, 1905, **87**, 819.
[4] *Phil. Mag.*, 1905, [vi], **10**, 1.
[5] *Amer. Chem. J.*, 1905, **34**, 1.
[6] *Ibid.*, 1902, **28**, 1.

pressure, owing to the slowness with which water passes through the membrane. A thermostat was not used, but in the later experiments the cell was enclosed in a felt-lined box. This secured a slow variation of temperature, but even on the same day the temperature change sometimes exceeded 1°, and on successive days the temperature varied by 3° or 4°. All the measurements were made in the vicinity of 20°.

The degree of accuracy which the authors attained may be exemplified by the following results for the molecular weight of cane sugar as deduced from the osmotic pressures observed with three solutions of the same concentration. The values in each column were obtained by noting the temperature and manometer readings from time to time.

Experiment I.	Experiment II.	Experiment III.
337·3	341·7	343·7
336·2	342·2	342·1
336·6	338·4	339·2
339·4	340·5	342·3
340·7	339·0	339·0
336·7	341·4	340·3
—	340·4	—
Mean..... 337·8	Mean..... 340·5	Mean..... 341·1
Range ... 4·5	Range ... 3·8	Range ... 4·7

General mean..... 339·8 Extreme range..... 7·5

Solutions of thirteen different concentrations were examined ranging from normal down to 1/20 normal. These solutions were made up by weight and the specific gravity of each solution used was carefully determined.

The authors' results may be summed up as follows: cane sugar, dissolved in water, exerts an osmotic pressure equal to that which it would exert if it were gasified at the same temperature in the volume, not of the solution, but of the pure water contained in the solution. Thus the solution which exerts an osmotic pressure at 0° of 22·4 atmospheres is not that which contains 1 gram-molecule or 342 grams of sugar in 1 litre of solution, but that which is made by dissolving 342 grams of sugar in 1 litre of water. It may be noted that the authors use in their calculations the gram-molecular volume for hydrogen as determined by Morley, namely, 22·488 litres, and not the normal value, 22·412 litres (p. 3).

A continuation of the measurements is promised in which the authors intend to devote particular attention to the following sources of error: (1) thermometer effects, (2) uncertainty as to volume at head of manometer, (3) sugar-inversion in the cell.

Thermochemistry.

T. W. Richards, L. J. Henderson, and G. S. Forbes [1] discuss the effect of thermometric lag and chance losses of heat in calorimetry, and propose methods for reducing these effects to a minimum. With a Beckmann thermometer, the effect of the lag will even in the most favourable circumstances exceed 0·001° and cannot therefore be neglected. The authors show how the correction may be determined graphically for each apparatus. The methods of both Rumford and Regnault-Pfaundler for getting rid of the effect of heat exchange with the environment, or allowing for this by calculation, practically assume a steady change of temperature of the calorimeter during the period of observation according to Newton's law. This is by no means in accordance with the actual occurrence in the calorimeter in many thermochemical determinations. The authors eliminate the error due to this uncertainty by altering the temperature of the surrounding bath in the same tempo as the alteration of temperature in the calorimeter proper, and give experimental details of the heat of interaction of sulphuric acid and caustic soda by the old and by the new methods. By the use of the latter it seems possible to determine the heat of such reactions when the temperature change is 3° with an accuracy of 0·1 per cent.

W. Jaeger and H. von Steinwehr [2] discuss the sources of error in determining heats of combustion in the calorimetric bomb, and give particulars for the electrical standardisation of the apparatus. They recommend the platinum instead of the mercury thermometer for all calorimetric work, as by its use the errors referred to by Richards are reduced to a minimum.

A controversy regarding the accuracy of the methods employed by Thomsen and Berthelot respectively for the determination of heats of combustion of organic compounds may be found in the pages of the *Zeitschrift für physikalische Chemie* and *Comptes rendus de l'Académie des Sciences* for 1905. The participators are Thomsen, Berthelot, and D. Lagerlöf. Thomsen contends that his method is more satisfactory than the bomb method as used by Berthelot, and points out that regularities are displayed in his heats of combustion for homologous series which are absent from those of Berthelot.

Julius Thomsen [3] gives in tabular form the heats of combustion at constant pressure and the heats of formation at constant volume of 120 volatile organic compounds. The heats of formation are given both with reference to amorphous carbon with the heat of combustion 96,960 cal., and to the "carbon atom." The second or "absolute"

[1] *Zeit. physikal. Chem.*, 1905, **52**, 551.
[2] *Ibid.*, **53**, 153; 1906, **54**, 428.
[3] *Ibid.*, 1905, **52**, 343.

heat of formation is derived from the first by the addition of 38,380 cals. for each carbon atom in the molecule.

The temperature-coefficient of the heat of neutralisation of some strong acids and bases has been determined by A. Wörmann.[1] At 0° he employed the ice-calorimeter ; at 6°, 18°, and 32°, the mixing calorimeter. He found that between 0° and 32° the heat of neutralisation could be accurately expressed by the simple formula

$$s = s_o - At,$$

whence

$$\frac{1}{s} \cdot \frac{ds}{dt} = \frac{A}{s},$$

that is, the temperature-coefficient of the heat of neutralisation increases with rise of temperature. The heat of neutralisation of potassium hydroxide is somewhat greater than that of sodium hydroxide, and the diminution with rise of temperature is less for potassium hydroxide than for sodium hydroxide. Between the heats of neutralisation of hydrochloric and nitric acid there is scarcely any difference. There is a sharp diminution of the heat of neutralisation between n and $n/2$ solutions, but nothing perceptible between $n/2$ and $n/10$.

C. Dieterici[2] gives the number $c_{0-100}/c_{15} = 1{\cdot}0020$ for the relation between the Bunsen mean calorie and the calorie at 15°. U. Behn[3] gives $c_{0-100}/c_{15} = 0{\cdot}9997$.

Photochemistry.

The relation between the absorption spectra of organic compounds (especially in the ultra-violet region) and their constitution continues to be systematically investigated.[4] In addition to the general principle that similarity in spectrum connotes similarity in structure, it is suggested that an absorption band appears wherever there is tautomeric change within the molecule. This hypothesis has been applied, so far with satisfactory results, to several cases of enol-keto-tautomerism, and to certain derivatives of benzene.

A study of the phosphorescent sulphides of the metals of the alkaline earths has led to the conclusion[5] that the phosphorescence is not a property of the pure sulphides, but arises from the presence of small quantities of the heavy metals dissolved in them. Iron and platinum are active in this respect, and the phosphorescence increases

[1] *Ann. Physik*, 1905, [iv], **18**, 775. [2] *Ibid.*, **16**, 593. [3] *Ibid.*, 653.

[4] J. J. Dobbie and C. K. Tinkler, *Trans.*, 1905, **87**, 269, 273 ; E. C. C. Baly and C. H. Desch, *ibid.*, 766 ; E. C. C. Baly and J. N. Collie, *ibid.*, 1332 ; E. C. C. Baly and E. K. Ewbank, *ibid.*, 1347, 1355.

[5] P. Waentig, *Zeit. physikal. Chem.*, 1905, **51**, 435.

with the quantity of them in the sulphide, provided that they remain in the state of solid solution and are not merely mixed with the sulphide.

A comprehensive paper on luminescence has been published by M. Trautz.[1] An historical survey of the work on crystallo-luminescence, triboluminescence, and chemiluminescence is given, and the results of many original observations in the domain are detailed. Of somewhat more than 800 substances which have been investigated, nearly 30 per cent. show triboluminescence when their crystals are crushed. The spectrum of the luminescence caused by chemical action is always continuous, even when the action is between gases.

Chemical luminescence is much more common in alkaline than in neutral or acid solutions.

Specific Heat and Equilibrium.

Attention was drawn in the Report for 1904 (p. 9) to two papers, by T. W. Richards and van't Hoff respectively, dealing with the effect of specific heat on equilibrium. These papers have been subjected to criticism by J. E. Trevor[2] and J. M. Bell,[3] chiefly from the mathematical side, and the following points in their critical discussion may be noted.

Helmholtz deduced the following general equation :

$$f - f_0 = (c - \eta_0)(\theta - \theta_0) - c\theta \log_e \frac{\theta}{\theta_0},$$

in which f denotes specific free energy, η specific entropy, c specific heat, and θ absolute temperature. The equation of van't Hoff is apparently identical with this, but is in reality incorrect on account of the meaning which he attaches to the terms. The reason is that van't Hoff integrates from $\theta = 0$ on the assumption that the difference of the specific heats of the system before and after the transformation is constant for all temperatures, an assumption which is not in general exact, and an arbitrary limitation imposed on Helmholtz's formula.

Richards' hypothesis that $\frac{\delta \Delta f}{\delta \theta} = M \frac{\delta \Delta e}{\delta \theta}$, where M is independent of θ, reduces to the assumption that isothermal changes of specific heat (by transformation) are proportional to a constant (the $1/M$th) power of the absolute temperature. This is another arbitrary limitation of Helmholtz's formula, and is not in accordance with the bulk of the experimental data available to test it.

[1] *Zeit. physikal. Chem.*, 1905, **53**, 1.
[2] *J. Physical Chem.*, 1905, **9**, 299.
[3] *Ibid.*, p. 381.

Trevor deduces thermodynamically the condition that

$$F\left(\frac{\delta\Delta e}{\delta\theta}, \frac{\delta\Delta f}{\delta\theta}\right) = 0,$$

and finds that it is satisfied by Richards' relation.

Transformation of Polymorphic Substances without Volume-change.

Generally speaking, the transition from one polymorphic modification to another is accompanied by change of volume. An exception will only occur when, according to Tammann, the neutral-volume curve, at all points of which the difference of the specific volumes of the two modifications is zero, cuts the transition-curve in the p-T-plane. That this should happen for a given substance in the neighbourhood of the atmospheric pressure is improbable. H. Steinmetz[1] points out that transition without volume-change must be a characteristic of Groth's polysymmetric substances, for in such cases the modifications are not physically distinct or ultimately different in crystalline structure, but differ merely in lamellar orientation of similar structures. The modifications can only show differences with regard to vector properties such as the optically uni- or bi-axial nature of the crystals.

The author has found examples of both types of substances. Sodium magnesium uranylacetate, $NaMg(UO_2)_3(C_2H_3O_2)_9,9H_2O$, when investigated with the dilatometer showed no perceptible change in volume, although it has a transition point at 27·5° under atmospheric pressure, the monoclinic pseudo-hexagonal substance becoming in reality hexagonal at that temperature. That this is a true transition may be deduced from the fact that the expansion-coefficients of the two modifications are different. At 50 atmospheres, the transition temperature is 30°. No heat-effect could be detected at the atmospheric pressure. Tammann's condition that the neutral curve should cut the transition curve is apparently here realised.

Chromglaserite, $K_3Na(CrO_4)_2$, affords an instance of a true polysymmetric substance. When heated between 150° and 175°, it gradually passes from complicated pseudo-hexagonal optically biaxial twins into uniaxial hexagonal crystals without perceptible change of volume (less than 0·006 per cent.). On cooling, it retains the hexagonal structure. Here there is no sharp transition point, and the temperature at which one or the other modification is produced depends on external circumstances. Water at 100° deposits the hexagonal form. The two modifications have the same coefficient of expansion, and are perfectly stable in each other's presence at the ordinary temperature.

[1] *Zeit. physikal. Chem.*, 1905, **52**, 449.

The Phase Equilibrium of Sulphur.

A. Smith with collaborators[1] has continued the investigation of the equilibrium of sulphur, which in the liquid state is highly abnormal. The theory to which the authors are led is as follows.

There are two forms of liquid sulphur which are only partially miscible; first, S_λ, the pale yellow, mobile liquid which is the more stable form up to 160°, and second, S_μ, the brown, viscous liquid which is the more stable form above 160°. All liquid sulphur contains both of these modifications up to high temperatures, the quantity of each present depending ultimately on the temperature only, as in ordinary transformations of liquid dynamic isomerides. Up to 160°, the equilibrium quantity of S_μ is completely dissolved by S_λ. At this temperature there are probably two phases: a saturated solution of S_μ in S_λ and a saturated solution of S_λ in S_μ. Above 160°, only the latter solution is stable, and the amount of S_λ present diminishes as the temperature rises. The establishment of the equilibrium $S_\lambda \rightleftarrows S_\mu$ is somewhat sluggish in the presence of certain foreign substances, for example, sulphur dioxide, traces of which are always present in ordinary sulphur, so that it is not difficult to obtain superheated or supercooled conditions. In particular, a large proportion of the S_μ present in the hot liquid may survive at the ordinary temperature if the liquid is suddenly chilled. It then forms the insoluble, non-crystalline variety known as amorphous sulphur. S_λ on cooling always forms crystalline sulphur. The freezing point of pure S_λ was found in two determinations to be 119·170° and 119·165° respectively. When sulphur is absolutely pure, no amorphous sulphur is obtained on rapidly cooling liquid sulphur from its own boiling point.

The only instance hitherto known of biphasic equilibrium between liquids in systems of one component is afforded by those substances which can exist as "fluid crystals."

Chemical Equilibrium involving Gases.

The equilibrium $2SO_2 + O_2 \rightleftarrows 2SO_3$ of the contact process for sulphuric acid has been carefully studied by M. Bodenstein and W. Pohl.[2] It was found that in presence of platinum sponge the equilibrium obeyed the formula derived from the law of mass action, namely,

$$K = \frac{C^2_{SO_2} \times C_{O_2}}{C^2_{SO_3}},$$

[1] *J. Amer. Chem. Soc.*, 1905, **27**, 797, 979; *Zeit. physikal. Chem.*, 1905, **52**, 602; 1906, **54**, 257.

[2] *Zeit. Elektrochem.*, 1905, **11**, 373,

with great accuracy. The experiments were conducted at various temperatures in a range from 528° to 897°, and from the equilibrium constants at different temperatures it was calculated from van't Hoff's formula that the heat of reaction is 21,700 cal. at about 700°, or, by extrapolation, 23,100 cal. at 15°. The value experimentally found by Berthelot is 22,600 cal. The agreement between theory and experiment is thus extremely close.

W. Nernst and H. von Wartenberg[1] have measured the dissociation of water and of carbon dioxide at high temperatures. The following table gives the percentage dissociation at the temperatures noted:

Water.			*Carbon Dioxide.*		
1124°.	1207°.	1288°.	1300°.	1400°.	1478°.
0·0078	0·0189	0·034	0·00400	0·0138	0·032

A. Jaquerod and F. L. Perrot[2] have determined the coefficients of expansion of nitrogen, oxygen, air, and the oxides of carbon between 0° and the melting point of gold (1067·4° on the nitrogen thermometer). Using their results to calculate vapour densities and thence molecular weights by D. Berthelot's process, they find values of the latter at 1067° agreeing with those at the ordinary temperature. This shows in particular that carbon dioxide cannot be dissociated to as great an extent as 0·02 per cent. at 1067°, in agreement with Nernst and Wartenberg's observation.

The temperature of the complete dissociation of the carbonates of the alkaline earths at 1 atm. pressure of carbon dioxide has been determined by O. Brill[3] by means of the microbalance with the following results:

$CaCO_3$.	$SrCO_3$.	$BaCO_3$.
825°	1155°	1450° (?)

The influence of metals on the reaction $2CO \rightleftarrows C + CO_2$ has been studied by R. Schenck and W. Heller.[4] Nickel and cobalt act as pure catalytic agents; iron, however, plays in addition a direct part in the action as soon as the pressure of carbon dioxide exceeds that required in the equilibrium between iron and the two oxides of carbon, and is oxidised by carbon dioxide into ferrous oxide. In presence of iron, ferrous oxide, and carbon, the oxides of carbon attain a fixed equilibrium pressure for each temperature, and the ratio of the partial pressures of the two oxides is also fixed. If the total pressure

[1] *Göttinger Nachrichten*, 1905, 35, 64.
[2] *Compt. rend.*, 1905, **140**, 1542.
[3] *Zeit. anorg. Chem.*, 1905, **45**, 275.
[4] *Ber.*, 1905, **38**, 2132, 2139; Smits, *ibid.*, 4027.

of the oxides exceeds this value, iron is oxidised and carbon deposited. The authors have measured the equilibrium pressure for various temperatures by two different methods which yield fairly concordant results. The pressure attains the value of 1 atm. at 775°; at 695°, it has a value of about 250 mm., which, in view of the presence of atmospheric nitrogen, is approximately the sum of the partial pressures of the oxides of carbon in the blast-furnace. Iron oxide will therefore be reduced in the furnace at all temperatures over 695°.

The authors have used the method of heating the various modifications of carbon with ferrous oxide and determining the equilibrium pressure in order to ascertain the relative stability of these modifications, the more stable modification at any temperature giving the lower pressure. They find the ascending order of stability between 400° and 800° to be (*a*) sugar charcoal, (*b*) diamond, (*c*) graphite and carbon from carbon monoxide, the two latter giving practically the same values.

H. B. Dixon[1] in a lecture delivered before the German Chemical Society gives an interesting account of his own work and that of his predecessors on combustion, explosion, and the explosive wave.

W. Nernst[2] has discussed the means for determining the point of equilibrium in explosions. For the most part the reaction velocities on completion of the explosion are so great that on cooling there is a great displacement of the equilibrium. In some cases, however, for example, the formation of nitric oxide from detonating mixture and air, the velocity of reaction is comparatively small. Here the maximum temperature is maintained for some time and then rapidly falls, so that the equilibrium is not greatly disturbed during the process of cooling. Applying the ordinary principles of chemical equilibrium to this example, the author finds that the theoretical results are in sufficient accordance with the experimental data of K. Finckh.[3] The determination of the maximum pressure of the explosion also yields satisfactory results.

Liquid Mixtures and Solutions.

W. Timofejeff has published in the *Izvestia* of the Kieff Polytechnic Institute, 1905, 1—340, an extensive report of his investigations on the heat of formation of liquid mixtures and non-aqueous solutions.[4] His object was to ascertain whether there existed any regular connection between the heats of formation of liquid mixtures and the physico-chemical nature of the components. The substances investigated were for the most part those which showed no great tendency to association either in themselves or with other substances.

[1] *Ber.*, 1905, **38**, 2419.
[2] *Zeit. anorg. Chem.*, 1905, **45**, 126.
[3] *Ibid.*
[4] Compare *Chem. Centr.*, 1905, ii, 429.

He gives a table of specific heats of eighteen organic liquids at 20° and the value of the temperature-coefficient at this temperature. From this table, it appears that the self-associative substances, with the exception of acetic acid, have the greatest temperature-coefficients. The specific heats of liquid mixtures were also studied, and from his observations the author is able to divide the mixtures into two well-defined groups. The first group consists of those mixtures the specific heats of which may be calculated from the specific heats of their components by the simple additive rule: the second group contains mixtures which show considerable deviations from the additive rule, in most cases positive, but in some negative. Speaking generally, the first group includes non-associative—normal—liquids, or feebly self-associative liquids: these exert no action on each other. To these, however, must be added mixtures of the strongly self-associative acetic acid with toluene, pyridine, and alcohol. The second group includes mixtures containing chloroform or strongly self-associative substances. The anomalous position of acetic acid is probably connected with its exceptionally small temperature-coefficient of heat capacity, which resembles that of normal liquids.

The author determined the heat of mixing of 133 pairs of liquids at various concentrations, and extrapolated from these results values of the molecular heat of solution at infinite dilution. Such heats are little affected by change of volume on mixing (as such) or by change in heat capacity. On the other hand, change of state (solution of a solid or gas), change of molecular condition (molecular association or dissociation, electrolytic dissociation), formation of additive compounds, and work of dilution (disgregation) play a great part in determining the total thermal effect. For example, the heat of solution of a solid is chiefly determined by the latent heat of fusion of the solid. In the case of mixtures of liquids, four typical combinations may be distinguished.

1. Mixtures of normal, chemically indifferent liquids.
2. Mixtures of self-associative with normal liquids without chemical action.
3. Mixtures of normal liquids with chemical action.
4. Mixtures of self-associative and chemically acting liquids.

To the first group belong mixtures of the hydrocarbons, halogen derivatives, acetone, ethyl acetate, and the like. Here the heat of solution is determined chiefly by the negative heat of dilution of the dissolved substance.

To the second group belong such mixtures as benzene and alcohol. When a small quantity of benzene is added to a large quantity of alcohol, the negative heat of dissociation of the associated molecules of alcohol is added to the negative heat of dilution of the benzene; for

very dilute solutions, the first term is practically negligible. When, on the other hand, a small quantity of alcohol is added to a large quantity of benzene, the associated alcohol molecules are to a great extent broken up, and there is a large negative heat effect due to this cause.

The chemical actions characteristic of the third and fourth groups generally determine a positive heat of reaction which outweighs any negative heat of disgregation. Chloroform behaves as a non-associative but chemically active liquid, giving in almost all mixtures a positive heat effect. The author is inclined to regard it as the acyl perchloride of orthoformic acid, the hydrogen remaining in the molecule having acquired distinctly acid properties by the accumulation of negative groups.

As has already been indicated, when an indifferent solid is dissolved in a normal indifferent liquid, the heat of solution observed is practically identical with the heat of fusion of the solid, and the author suggests that when the heat of fusion of a solid cannot be directly observed it may be determined by ascertaining the heat of solution, preferably in a normal liquid, as much solid as possible being dissolved in the liquid so as still further to minimise the comparatively small heat of disgregation. Thus, the molecular heat of fusion of naphthalene is $-4{\cdot}6$ Cal.; its heat of solution for medium concentrations is given in the following table:

Solvent.	Ethyl acetate.	Benzene.	Methyl alcohol.	Ethyl alcohol.	Propyl alcohol.	*iso*Butyl alcohol.
Mol. heat of solution...	$-4{\cdot}1$	$-4{\cdot}4$	$-4{\cdot}7$	$-4{\cdot}7$	$-4{\cdot}9$	$-5{\cdot}1$

In connection with this thermal research, reference may be made to a paper by C. Forch[1] on the volume relations of naphthalene in solution. From measurements of the volume, and the change of volume with temperature, of two solutions having different concentrations, the volumes and temperature-coefficients of solvent and solute may be calculated. The molecular volume of naphthalene in toluene, chloroform, and carbon disulphide varies from 123·3 to 125 at 18°. The molecular volume of solid naphthalene at this temperature is 109·4, from which may be calculated the value of 125·7 as the molecular volume of the liquid substance at the same temperature. It thus appears that the volume of the naphthalene in these solutions is only slightly less than the volume which would be occupied by liquid naphthalene at the same temperature, or, in other words, that liquid naphthalene would mix with these solvents without appreciable contraction. The temperature-coefficient of the dissolved naphthalene is also very nearly that of liquid naphthalene, and many times greater than that of solid naphthalene. In ether, the molecular volume of naphthalene varies from 114 to

[1] *Ann. Physik*, 1905, [iv], **17**, 1012.

117·5. There would thus appear to be a considerable contraction on the mixing of liquid naphthalene with liquid ether.

I. Zoppellari [1] finds that the simple mixing formula applies with close approximation to the refractive power of solutions of naphthalene in benzene.

Colloidal Solutions.

A great many papers have been published during the year on this subject, the importance of which to biological and technical chemistry is now fully realised. There is still marked diversity of opinion as to the nature of such solutions, but accumulation and discussion of data would seem to be gradually leading to the notion that between solutions of crystalloids and solutions of colloids there are numberless gradations, so that while the extremes may be so different as to present no similarity in properties, it is yet impossible to draw a sharp line anywhere between them.

An interesting account of the fundamental data and principles of the subject is given by A. A. Noyes [2] in his presidential address to the American Chemical Society, in which he gives directions for the conduct of well-selected illustrative experiments. He thinks it convenient to distinguish between "colloidal solutions" and "colloidal suspensions." The former, for example, gelatine solution, are much more viscous than water; the latter, for example, arsenious sulphide solution, are not. The former gelatinise on cooling or evaporation, and pass again into solution on heating or on addition of solvent; the latter do not gelatinise on cooling, and if gelatinised by other means do not redissolve on heating. The former are not coagulated by the addition of moderate amounts of salt; the latter immediately give an abundant precipitate. Solutions of the first class exhibit osmotic pressure and diffusibility; solutions of the second class do not to any measurable extent. Colloids of the first class, though freely permeable to crystalloids, are impermeable to colloids of either class, and exercise a protective influence on colloids of the second class with regard to their coagulation by electrolytes. The abnormal viscosity of colloidal mixtures of the first class is probably always due to physical heterogeneity.

When an insoluble substance is formed by the interaction of two chemical compounds in the absence of electrolytes, it almost invariably separates as a colloidal suspension. The particles in suspension may be of almost any degree of fineness. Some may be visible to the microscope, others only to the ultramicroscope (which can detect particles 0·00001 mm. in diameter). The scattering of light and the

[1] *Gazzetta*, 1905 **35**, [i], 355. [2] *J. Amer. Chem. Soc.*, 1905, **27**, 85.

polarisation of the reflected light may yield inconclusive results, since Lobry de Bruyn has shown that true solutions, such as that of cane sugar, may to some extent exhibit diffuse reflection of polarised light, though in a much less degree than that of known suspensions.

With regard to the electrification of the particles in suspension, the sign of the charge of which may be determined from the direction of their migration towards electrodes, it may be noted that practically only basic hydroxides migrate towards the cathode; nearly all other substances migrate towards the anode, that is, they are negatively charged. Hardy's observation that the charge of suspended egg-albumin depends on whether the liquid in which it is suspended is acid or alkaline, may be explained from the fact that albumin is an amphoteric substance, capable of acting as base towards acids and as acid towards bases. The author thinks it possible that the charge of larger particles may be due to contact electricity, but that the charge of smaller particles is ionic. In the first case, the charge of opposite sign would reside in the solvent itself, in the second case it would appear on another ion. It seems highly probable that particles remain in suspension on account of their electrification; when they are discharged, they coagulate. Thus, suspensions of opposite sign are mutually precipitated when mixed, whilst those of the same sign are indifferent to each other. It is probable that the coagulation by means of an electrolyte is primarily due to the ion of charge opposite to that of the particles, and it would appear to be a function of the valency of this ion, bivalent ions being much more active than univalent ions, and so on.

A. P. Mathews[1] gives a more detailed theory of the coagulation of colloidal suspensions by electrolytes. He attributes the chief effect of the electrolyte to the change in surface-tension which it brings about in the suspended particles. The ion of the same sign as the particle tends to keep it dissolved, the ion of opposite sign to precipitate it. The total action of an electrolyte depends, therefore, on whether the action of the anion or cation preponderates. The author suggests the following formula for the "tension-coefficient" of the electrolyte: $\pi = \frac{E_a - E_c}{E_a + E_c}$. E_a and E_c are the electrolytic solution tensions of anion and cation respectively. The coagulating power of the electrolyte for a given colloid will depend on the sign and magnitude of this expression. The author has performed numerous experiments on the coagulation of egg-albumin by electrolytes and finds good agreement with his theory. He attributes the great effect of the valency of the active ion to the possibility of a multivalent ion acting as a link in an ion-colloid chain, and thus forming large

[1] *Amer. J. Physiol.*, 1905, **14**, 203.

accumulations which readily coagulate, whilst in the case of univalent ions no such chain-combination is possible.

C. Galeotti[1] points out that the precipitation of egg-albumin by ammonium sulphate is reversible, and has constructed the isothermal equilibrium curve for 15°.

J. Billitzer[2] also writes an interesting article on the theory of colloids, and treats in particular of their reciprocal coagulation. His general point of view may be given as follows. All solutions with charged particles or ions are of the same character, and only differ in the ratio of charge to mass. The simplest case is that of a completely ionised binary electrolyte ; here the charge is great compared with the matter associated with the charge. A feebly dissociated binary electrolyte forms the next stage. In such cases, we are accustomed to regard the charge as being entirely associated with the ions. The author, however, refers the small charge to the whole matter in solution, ionised and non-ionised. If the anion A' of the feeble electrolyte $C^{\cdot}A'$ is very small compared with the cation $C^{\cdot}$, and if, further, the latter is associated in a complex with non-ionised molecules CA to form $n(CA)+C^{\cdot}$, then the cation may cease almost to resemble an ordinary cation, and assume properties resembling those of an electrode (or suspended charged particle). Adopting this point of view, the author accounts in a simple way for many of the observed phenomena, and adduces fresh experimental matter in support of his theory. Amongst other things, the author shows experimentally that the optimum of precipitation of oppositely charged colloidal suspensions is attained when those quantities of the colloids are taken which carry equal amounts of electricity. The method adopted by the author to ascertain the ratio between charge and mass of a given colloid is to precipitate it with a suitable salt and analyse the filtered liquid. Thus a colloidal solution of arsenious sulphide was precipitated with barium chloride, and in the filtrate, barium, chlorine, and free acid were estimated. The barium and chlorine were originally in equivalent proportions ; after treatment with the colloid, the barium is no longer equivalent to the chlorine in the solution, and the difference gives the amount of barium which has been carried down in the precipitate. The positive charge on this amount of barium went to neutralise the negative charge on the colloidal particles of the arsenious sulphide, and thus the ratio of charge to mass is determined.

Another method of determining the charge associated with a given amount of colloid is described by J. Duclaux.[3] He determines the electrical conductivity of the colloidal solution, and then that of the

[1] *Zeit. physiol. Chem.*, 1905, **44**, 461.
[2] *Zeit. physikal. Chem.*, 1905, **51**, 129.
[3] *Compt. rend.*, 1905, **140**, 1468.

liquid after filtration through collodion. The difference gives the conductivity due to the colloidal particles retained by the collodion. He calculates that the charge of a gram-equivalent of colloidal ferric hydroxide is about 0·002 of that of a univalent ion. From Billitzer's experiments, the value 0·025 may be calculated. Duclaux has also made measurements of osmotic pressure, with collodion as semipermeable membrane.[1] His measurements agree roughly with his conductivity results.

E. Waymouth Reid[2] has measured the osmotic pressure of carefully purified hæmoglobin at 15°, using a gelatine membrane, which is impermeable to the dissolved substance. In seven experiments, he obtained values of the osmotic pressure varying from 3·51 to 4·35 (mean 3·86) millimetres of mercury for a 1 per cent. solution of hæmoglobin. This corresponds to a molecular weight of about 45,000. It is noteworthy that the specimens of hæmoglobin employed gave optically void solutions, as judged by the ultramicroscope.

With reference to the experiments of Ramsden,[3] attention may be drawn to a paper by W. V. Metcalf[4] on solid peptone films formed on the surface of water. These films are not due to oxidation, as they are formed with equal readiness in an atmosphere of hydrogen. They permit the free evaporation of water, and generally increase in strength with lapse of time, sometimes, however, passing through a maximum and a minimum. The minimum weight of peptone which is requisite for such a solid film is 4×10^{-7} gram per sq. cm., and the probable minimum thickness is 3×10^{-6} mm. The author considers the experimental results to be an illustration of Gibbs's thermodynamic principle that when a possible chemical action in a solution would lead to a diminished surface-tension, then there is a tendency for this action to occur in the surface layer of the liquid, and if the product of the action is insoluble a surface-film results.

Reciprocal Salt-pairs.

W. Meyerhoffer[5] has made a detailed study of the heterogeneous equilibrium,

$$BaSO_4 + K_2CO_3 \rightleftarrows BaCO_3 + K_2SO_4,$$

both from the practical and theoretical points of view. The subject is treated by him as a problem in reciprocal salt-pairs rather than as a problem in mass-action. This new method of treatment has led to a much more thorough understanding of the case than has hitherto been possible. The classical research of Guldberg and Waage on the subject was concerned only with the equilibrium attained when the solid

[1] *Compt. rend.*, 1905, **140**, 1544.
[2] *J. Physiol.*, 1905, **33**, 13.
[3] *Ann. Reports*, 1904, p. 12.
[4] *Zeit. physikal. Chem.*, 1905, **52**, 1.
[5] *Ibid.*, **53**, 573.

phase consisted of the two barium salts alone, the potassium salts being entirely in solution. This equilibrium curve is only one of four possible curves in an isothermal diagram, of which the axes serve to measure molecular concentrations of potassium carbonate and potassium sulphate respectively. The other curves refer to

a. barium carbonate, potassium carbonate,
b. barium carbonate, potassium sulphate,
c. barium sulphate, potassium sulphate,

as solid phases respectively. The four curves represent bivariant systems, and cut one another and the axes in four points which represent univariant systems, two of which have a solid phase of three salts.

In a former research, the author showed that on fusion the system $BaCO_3,K_2SO_4$ is stable, and the system $BaSO_4,K_2CO_3$ metastable. He now proves that at the ordinary temperature in presence of water the first system retains its stability.

According to Guldberg and Waage, the concentrations of potassium carbonate and potassium sulphate simultaneously in equilibrium with the barium salts as solid phase at 100° bear a constant ratio to each other independently of the total concentration. This the author shows to be inaccurate at 100°, and still further from the truth at low temperatures. The figures he obtains are as follows:

25°.		80°.		100°.	
ΣK_2.	K_2CO_3/K_2SO_4.	ΣK_2.	K_2CO_3/K_2SO_4.	ΣK_2.	K_2CO_3/K_2SO_4.
32·32	9·03	35·16	2·72	35·65	1·82
11·17	15	8·30	4·4	8·3	3·1
4·0	21	4·0	5·1	4·0	3·7

ΣK_2 represents the total number of gram-molecules of potassium salts dissolved in 1000 gram-molecules of water. According to the theory of electrolytic dissociation, the constant ratio should be CO_3''/SO_4''. The data for testing this deduction are, however, wanting.

The author discusses in detail the experimental and analytical methods employed by Dulong, Rose, and Guldberg and Waage, and shows that in each case the results obtained by them were at best only approximately correct. Generally speaking, sufficient time was not allowed by these experimenters for the proper attainment of equilibrium The measurements by Guldberg and Waage at 100° are the most satisfactory, and the author points out that, when the experiments are arranged in descending order of total concentration of potassium salts there is a well-marked increase in the ratio K_2CO_3/K_2SO_4, in accordance with his own results.

Non-aqueous Electrolytic Solutions.

J. H. Mathews[1] has measured a number of dielectric constants of liquids previously undetermined, and presents a practically complete bibliography of the subject. From a discussion of the data, he concludes that the Nernst-Thomson rule of the correlation of dissociating power and dielectric constant has no foundation in fact, and that the exceptions are as numerous as the confirmations.

The abnormal variation of electrical conductivity in non-aqueous solution is the subject of a paper by B. D. Steele, D. McIntosh, and E. H. Archibald,[2] in connection with their work on the halogen hydrides as conducting solvents. They show that if (1) an ionisable compound of n molecules of solute with m molecules of solvent, or (2) an ionisable n-fold polymeride of the solute, is formed, then, if no ions are produced from simple molecules of the solute, the molecular conductivity will be $\mu = \alpha K' a^{n-1}$ where a is the simple concentration of the solute, K' a constant, and α the ionisation coefficient of the ionisable complex. Although the molecular conductivity referred to the simple solute may diminish with increasing dilution, the molecular conductivity referred to the complex ionisable solute will increase. The conduction of organic compounds in the liquefied halogen hydrides is best explained by the occurrence of ionisable compounds of solute with solvent. Transport numbers show that the organic substance is carried to the cathode as a component of a complex cation.

P. Dutoit and A. Levier,[3] in view of the discrepancies between the numbers of various observers for the conductivity of salts dissolved in acetone, have made careful measurements of the conductivity of the bromides, iodides, and thiocyanates of lithium, sodium, potassium, and ammonium in this solvent at 18°. The lowest value for the conductivity of acetone which they obtained was $0{\cdot}23 \times 10^{-7}$ reciprocal Siemens units. With unplatinised electrodes, concordant readings could be obtained up to a resistance of 1,000,000 ohms. The range of dilution studied was from 100 to 100,000. In every case it was found that the molecular conductivity increased with the dilution to reach a constant value as in water. Kohlrausch's law of the additive nature of the maximum molecular conductivity holds good with close approximation. The ionic velocities of the cations are nearly equal, those of the anions differ considerably.

For very dilute solutions ($v > 1000$), Ostwald's dilution law seems to be obeyed; for greater concentrations, the dissociation constant

[1] *J. Physical Chem.*, 1905, **9**, 641.
[2] *Phil. Trans.*, 1905, **205** *A*, 148.
[3] *J. Chim. Phys.*, 1905, **3**, 435.

diminishes with increasing dilution. On the whole, the resemblance to aqueous salt solutions is close.

By simultaneous measurements of solubility and electrical conductivity, H. F. Sill [1] has studied the equilibrium between cinchonine and various acids dissolved in methyl or ethyl alcohol. From his observations, the affinity constants of the acids could be calculated, and it was found that these constants are practically proportional to those found for aqueous solutions.

Hydrates in Aqueous Electrolytic Solution.

J. Domke and W. Bein [2] have made fresh determinations of the density and expansion of aqueous sulphuric acid solutions, and employ their experimental results for the purpose of ascertaining whether they afford information as to the presence of definite hydrates in solution. The authors' determinations are in excellent agreement with those of S. U. Pickering. They are of opinion that a consideration of the density alone can lead to no adequate conclusion as to the hydrates existing in solution. From a consideration of other physical evidence, however, they think that the hydrate $H_2SO_4 + H_2O$ most probably exists—hydrates with $2H_2O$, $4H_2O$, and $6H_2O$ are less certain. In dilute solutions there is no direct proof of the existence of hydrates to be derived from a consideration of the numerical values of specific physical properties. The authors give a systematic bibliography of papers bearing on the existence of hydrates in solution.

A useful discussion of the modern physico-chemical data which may be interpreted with reference to the hydrate theory of aqueous solutions may be found in a paper by T. M. Lowry.[3] The fundamental assumption of the author is that the ions in an aqueous electrolytic solution are together more highly hydrated than the non-ionised substance in its highest stage of hydration. Thus it is only at very high dilutions that complete ionisation is possible. The general nature of ionising solvents, the influence of temperature on ionisation, the comparison of the mobilities of different related ions in aqueous solution, the influence of temperature on these mobilities,[4] and the freezing points of dilute aqueous solutions (Biltz ; Jones and Getman), all point to the ions of salts being for the most part highly hydrated. The phenomena of autolytic conduction and the special case of caustic soda [5] are also discussed.

H. Jahn [6] has made accurate determinations of the freezing point

[1] *Zeit. physikal. Chem.*, 1905, **51**, 577.
[2] *Zeit. anorg. Chem.*, 1905, **43**, 128.
[3] *Trans. Faraday Soc.*, 1905, **1**, 197.
[4] *Ann. Reports*, 1904, p. 17.
[5] W. R. Bousfield and T. M. Lowry, *Phil. Trans.*, 1905, **204** *A*, 289.
[6] *Zeit. physikal. Chem.*, 1905, **50**, 129.

depressions of some alkaline chlorides and bromides, which on the whole agree well with those of previous observers. For sodium and potassium chlorides, there is concordance between the ionisations deduced from the freezing points and from conductivity values. For lithium chloride, the conductivity gives smaller, and for cæsium chloride and potassium bromide greater, ionisations than the freezing-point method. If somewhat smaller values for Λ_∞ are used than those given by Kohlrausch, satisfactory dilution constants are obtained from the conductivities of dilute solutions. The author develops somewhat complicated formulæ for solutions which give good concordance with experimental data in various directions. He regards $\gamma = \Lambda/\Lambda_\infty$, van't Hoff's freezing-point expression, and the expression for the *E.M.F.* of concentration cells as limiting expressions, never actually fulfilled.

H. C. Jones and H. P. Bassett [1] give a *résumé* of their work on the composition of hydrates in solution, as deduced from the freezing point, boiling points, conductivity, &c., of the solutions.

Mobility of Ions.

It has been found by Tijmstra [2] that in a methyl-alcoholic solution the ion $-O\cdot CH_3$ moves more rapidly than the ion OH'. H. Danneel [2] considers this fact in conjunction with the comparatively great velocities of $H^{\cdot}$ and OH' in water, and suggests that the speed of ions may appear to be much greater than they are in reality when these ions are moving amongst undissociated molecules from which they may be produced. Thus a hydrogen ion moving in water may, by meeting a non-ionised water molecule, itself lose its ionic character and liberate one of the hydrogen atoms of the water molecule as a charged ion. If the time required for this interchange is less than that which would be occupied by the original ion in traversing a distance equal to the diameter of the water molecule, then the apparent speed of hydrion as measured from conductivities, &c., will be greater than its real speed. The author applies this idea to the consideration of the conductivities of salt solutions. In a concentrated solution, with many non-ionised salt-molecules, the interchange will occur much more frequently than in dilute solutions, so that in the former the ionisation, as measured by the molecular conductivity, will give too high results owing to the greater apparent mobility of the ions. The formula used by the author to deduce the "real" molecular conductivity Λ' from the apparent molecular conductivity Λ is $\Lambda' = \Lambda - 180N$, where N is the molecular concentration (normality). He obtains results for potassium and

[1] *Amer. Chem. J.*, 1905, **34**, 290.
[2] *Zeit. physikal. Chem.*, 1904, **49**, 345.
[3] *Zeit. Elektrochem.*, 1905, **11**, 249.

sodium chlorides in good agreement with Jahn's cryoscopic measurements (p. 23).

W. R. Bousfield [1] deals with ionic sizes in relation to the conductivity of electrolytes. By assuming hydration of the ions and the applicability of Stokes's law to the motion of the ions, the author deduces the following formula for the true coefficient of ionisation for potassium chloride:

$$\alpha = \frac{\Lambda}{\Lambda_\infty} \cdot \frac{1}{f} \cdot \frac{1}{1+3{\cdot}33h^{-0{\cdot}667}},$$

in which Λ is the molecular conductivity, f the fluidity of the solution, and h the hydration, that is, the ratio of the molecules of water present to the molecules of the solute.

Increased Solubility due to Diminished Ionisation.

The solubility of magnesium hydroxide in solutions containing ammonium chloride is usually accounted for on the hypothesis of electrolytic dissociation by the diminution of the hydroxidion concentration caused by the formation of the feeble base, ammonium hydroxide. J. C. Philip [2] has investigated a series of similar instances in the influence of various sodium salts on the solubility of sparingly soluble acids: the acids chosen were cinnamic, benzoic, salicylic, and nitrobenzoic acids, the sodium salts being acetate, butyrate, formate, and salicylate. The electrolytic dissociation theory leads under the usual simplifying assumptions to the expression

$$C_a^2 = \frac{p}{k'}(S - C_a),$$

in which S is the molecular concentration of the sodium salt added, p the solubility product of the acid HA, k' the dissociation constant of the acid HA', corresponding to the sodium salt employed, and C_a the concentration of the anion A, which may be taken as the measure of the increased solubility of the acid HA. It is therefore possible to calculate C_a for any given S when p and k' are known. The author finds excellent agreement between calculation and experiment when the solutions of sodium salts used are not too concentrated, that is, do not greatly exceed 1/20-normal.

Another example of increase in solubility due to diminution of ionisation has been studied by A. A. Noyes and W. H. Whitcomb.[3] It is well known that lead sulphate dissolves readily in a concentrated solution of ammonium acetate. This increased solubility might either be due to the formation of complex cations containing lead, or to the

[1] *Proc. Roy. Soc.*, 1905, **74**, 563; *Zeit. physikal. Chem.*, 1905, **53**, 257.
[2] *Trans.*, 1905, **87**, 987. [3] *J. Amer. Chem. Soc.*, 1905, **27**, 747.

lead acetate formed by metathesis being only slightly ionised. By an investigation of the conductivity of lead acetate solutions and of the ionic migration in solutions of lead sulphate in ammonium acetate, it was proved that the increased solubility is mainly due to the relatively small ionisation of lead acetate. In decinormal solution in pure water, lead acetate is only about 20 per cent. ionised. In solutions containing much ammonium acetate, practically all the lead is in the non-ionised condition. The solubility of the lead sulphate is roughly proportional to the concentration of ammonium acetate in the solution.

A Rapid Hydrion Catalysis.

A catalytic method for measuring small concentrations of hydrion, whether existing in very dilute solutions of strong acids or in more concentrated solutions of feeble acids, has hitherto been wanting. The catalysis of methyl acetate or of cane sugar at laboratory temperatures proceeds so slowly when the hydrion concentration is in the region of $N/100$ that the methods are practically useless.

G. Bredig and W. Fraenkel have now made a preliminary communication[1] on a catalytic action due to hydrion, which proceeds at an incomparably greater rate than these and admits of accurate and easy measurement. The action is the decomposition of ethyl diazoacetate according to the equation

$$N_2{:}CH{\cdot}CO_2{\cdot}C_2H_5 + H_2O = CH_2(OH){\cdot}CO_2{\cdot}C_2H_5 + N_2,$$

and its velocity may be determined by measuring the volume of nitrogen evolved at suitable intervals. The action proceeds according to the unimolecular formula, and the value of the unimolecular constant k is at any temperature proportional to the hydrion concentration.

At 25°, the action proceeds so rapidly that under the influence of a $N/1000$ solution of a strong acid the decomposition has gone half-way in twenty minutes. The authors have succeeded in obtaining good velocity constants (showing a variation of less than 2 per cent. from the mean value) with $N/2000$ solutions. It is even possible to obtain velocity constants with $N/1000$ solutions of acetic and similar feeble acids. With such small concentrations, it is necessary to use platinum or well-steamed Jena glass vessels.

It is noteworthy that the strong acids do not give exactly the same relation between velocity constant and hydrion concentration as the weak acids. Thus, for nitric and picric acids, the ratio is 34·9 ; for acetic, succinic, and benzoic acids it is 32·5.

Neutral salts, when present in only very small proportions, exert

[1] *Zeit. Elektrochem.*, 1905, **11**, 525.

little direct influence on the catalysis, but at greater concentrations they give rise to reactions superposed on the simple catalytic action of hydrion.

Action of Ferments.

H. Euler[1] gives a summary of recent work on the catalytic action of ferments. He classifies provisionally the actions considered into those which take place in apparently homogeneous solutions and those which proceed in systems obviously heterogeneous. In tabular form, he gives the characteristic velocity constants for the different ferments, the influence of the concentration of the ferment as expressed by the formula $n = \frac{\log k_1 - \log k_2}{\log c_1 - \log c_2}$, and the influence of the concentration of the catalyte. The theoretical formulæ of V. Henri and of Herzog are discussed and criticised. In the author's opinion, the most probable assumption to account for the observed phenomena is the partial combination between ferment and catalyte, which may possibly resolve itself into the distribution of the catalyte between the aqueous solution proper and the ferment (colloidal phase).

A. W. Visser[2] has studied the catalytic action of invertase on cane sugar and of emulsin on salicin. His experiments seem to show that both actions are reversible, but the application of the proper velocity equations for the balanced actions leads to no better agreement with experimental data than is found when the simple equations for irreversible actions are employed. His mathematical treatment of the velocity-numbers is as follows. He assumes that in the reactions the law of mass action is strictly obeyed, and that the apparent divergence from the theoretical results arises from the changing "intensity" of the catalyst. From the experiments, he deduces an expression for the intensity as a function of the initial concentration of the catalyte and the concentration at the moment considered. Since the velocity of both direct and reverse actions at a given time is proportional to the intensity of the catalyst at that time, he multiplies the right-hand member of the velocity equation by the expression for the intensity, and thus obtains the complete velocity equation, which may then be integrated. Satisfactory constants are obtained in this way. In the range from 0° to 25°, a rise of 10° doubles the value of the constant for the inversion of cane sugar by invertase.

G. Senter[3] is of opinion that a study of temperature-coefficients of reaction velocities affords the best means of ascertaining the

[1] *Zeit. physiol. Chem.*, 1905, **15**, 420.
[2] *Zeit. physikal. Chem.*, 1905, **52**, 257.
[3] *J. Physical Chem.*, 1905, **9**, 311.

relative importance of the *rôles* played by chemical action and diffusion in determining the actual velocity in a colloidal solution.[1] For a 10° rise of temperature, the rate of diffusion increases about 1/4 of its value, whilst the rate of chemical action is approximately doubled. He gives a complete table of the influence of temperature on the velocities of enzyme reactions. The increase for 10° varies from 60 to more than 300 per cent.

Alternate Current Electrolysis.

M. Le Blanc[2] gives an account of some electrolytic experiments carried out with alternating currents. The problem to be solved may be stated thus. Copper cannot be deposited from potassium copper cyanide solution by means of a direct current, owing to the absence of cuprion and the stability of the complex cyanide ion containing copper. On the other hand, a copper anode in a solution of potassium cyanide easily dissolves when a current is passed. If, now, two copper electrodes are immersed in a cyanide solution and an alternating current is passed between them, will copper pass into solution? This should depend on whether the copper dissolved at the anode has or has not time to be converted into the complex ion before the reversal of the current. Once the complex ion is formed, the copper contained in it remains permanently in the solution. With a current density of 4·6 amperes per sq. dcm. and 4*N* potassium cyanide, the author found that if the rate of reversal was 1000 per minute the copper passed into solution quantitatively as if a direct current had been employed, whilst with a rate of 38,000 reversals per minute only 33 per cent. of the theoretical quantity dissolved. From this, the author concludes that in 0·001 minute the reaction between the copper ions and the potassium cyanide is practically completed, whilst in 0·0000013 minute the action cannot have proceeded to any measurable degree. By this method, the author hopes to gain information regarding the hitherto unknown rate of ionic reactions.

Brochet and Petit[3] do not share the view that the possibility of alternate current electrolysis depends on the formation of a complex ion, as in the above instance. They conceive the general condition for the formation of a new compound (whether gas, precipitate, or dissolved substance) to be that the ion on reaching an electrode has had time to part with its charge before reversal produces the ion of opposite charge at the same electrode.

In order to ascertain whether any special action accompanied the em-

[1] Compare *Ann. Reports*, 1904, p. 14.
[2] *Zeit. Elektrochem.*, 1905, **11**, 705.
[3] *Ibid.*, 1904, **10**, 909 ; 1905, **11**, 441.

ployment of an alternating current when no formation of complex ions was possible, Le Blanc studied the action between copper electrodes immersed in copper sulphate solution. With a symmetrical alternating current, nothing could be observed. With an unsymmetrical alternating current, that is, one with the periods of alternation such that the current flows for a longer time in one direction than in the other, it was found that the weight of one electrode increased by the same amount as that of the other diminished, quite independently of the rate of alternation, which varied from 3000 to 15,000 per minute. This behaviour indicates that no action different from that produced by a direct current here takes place.

The author observed that normal results with copper electrodes could only be obtained when the copper was definitely crystalline. When the electrode was heated to its melting point in the blowpipe flame and suddenly quenched in alcohol, it lost less in weight with an alternating current than the other electrode gained. It thus behaved as a more "noble" metal than normal crystalline copper, to which it slowly reverted. The passivity here observed could scarcely be due to the formation of a film of oxide, and is referred by the author to a low reaction velocity.[1]

JAMES WALKER.

[1] Compare *Ann. Reports*, 1904, p. 27.

INORGANIC CHEMISTRY.

Again we have to record losses in the ranks of the workers in inorganic chemistry; by the death of Cleve, our Society has lost one of its distinguished honorary Fellows, and chemistry a foremost worker in the department of the rare earths. Cleve was born at Stockholm on February 10th, 1840, received his early chemical training at the University of Upsala, where for three years, namely, 1863–66, he discharged the duties of "Privat-docent" in organic chemistry. Relinquishing this post, Cleve devoted some years to travel and to the completion of his chemical training, remaining for some time in Paris to study under Berthelot and Wurtz. These years of travel were useful in other ways, and reveal the many-sided scientific man, who was not only a chemist but also geologist and botanist. In 1870, Cleve was appointed to the staff of the Polytechnic at Stockholm, and in 1874 he became the professor of chemistry in the University at Upsala, in which position he continued until his death, which took place on June 18th. Cleve's published work, whilst it shows his activity in different departments of chemistry, both organic and inorganic, is chiefly concerned with the elucidation of the chemistry of the rare earths; in recognition of the importance of these investigations the Royal Society awarded him the Davy Medal in 1904. There is still one other association with the name of Cleve which recent events have emphasised, and that is to be found in the name cleveite given by Nordenskjöld to a species of pitchblende in which Sir William Ramsay first found a source of terrestrial helium.

On January 13th, T. H. Behrens, professor at the Polytechnic School at Delft, died at the age of 63. The name of Behrens is identified with micro-chemical analysis, to the perfecting of the methods of which branch of analysis he devoted much labour.

The death of G. B. Buckton on September 25th at the advanced age of 88 recalls the important investigations made between forty and sixty years ago on several members of that interesting group of substances, the metallo-organic compounds.

It is difficult, if not impossible, to give in a few words an indication of the direction of chemical research in inorganic chemistry during the

year. The number and variety of the elements themselves and their numerous compounds are largely responsible for the miscellany-like impression which the contemplation of the titles of the papers published produces. The exact revision of atomic weights has provided precise information in the case of some thirteen or fourteen elements. The commercial production of metallic calcium, chronicled last year, has provided the opportunity for the closer study of the chemical and physical properties of this element. Again, this year, we see another rare element pressed into the service of man; the electrolytic decomposition of tantalum tetroxide has been employed as a means of obtaining the metal in the form of filaments suitable for the construction of incandescent electric lamps. Such lamps have a useful life about the same as those with a carbon filament, whilst the electrical energy consumed is about one-half. A considerable number of papers deal with investigations of the rare earths. The application of physical methods, more especially the construction of fusion diagrams by Tammann's method, has very materially extended the knowledge of alloys, and in many instances afforded indications of the nature of the definite compounds formed by metals with one another. The study of colloidal solutions of metals and their compounds is another branch of investigation to which many chemists have devoted themselves during the year.

Atomic Weights and the Classification of the Elements.

In a paper entitled "A Contribution to the Development of the Periodic System," Werner[1] has suggested an arrangement of the elements for which many advantages over the generally accepted forms may be claimed. In this table, the elements are arranged horizontally in eight periods or series, the periods fall again into four sets of two each; in each set there are the same number of elements. In the first period, which might be styled the zero-period, there are three blank spaces, in which possibly "coronium" and "the ether" may find a place. The second period, a repetition of the first so far as the number of elements is concerned, contains at present hydrogen at one extreme and helium at the other, with a blank space next to helium representing the position of a lower homologue of the halogen group. The third and fourth periods contain a like number of elements, namely, eight; the third begins with lithium, the homologue of hydrogen, followed by glucinum, boron, carbon, nitrogen, oxygen, fluorine, and ends with neon, the next homologue of helium. In this period, the average difference in atomic weights from member to member is 1·85. The fourth period is constituted of the elements arranged in the order of their atomic weights, from sodium to argon, with sodium placed below

[1] *Ber.*, 1905, **38**, 914.

–																
H 1·008																
Li 7·03																
Na 23·05																
K 39·15	Ca 40·1															Sc 44·1
Rb 85·4	Sr 87·6															Y 89·0
Cs 133	Ba 137·4	La 138	Ce 140	Nd 143·6	Pr 140·5	–	–	Sa 150·3	Eu 151·79	Gd 156	Tb 160	Ha 162	Er 166	–	Tu 171	Yb 173·0	–
–	Ra 225	La a ?	Th 232·2	–	–	–	–	–	U 239·5	–	–	–	–	–	Ac ?	–	–

lithium, magnesium below glucinum, aluminium below boron, and so on, argon coming into the helium group.

The fifth and sixth periods are again constituted of a like number of elements, more numerous than the preceding periods, and contain eighteen elements each. In the fifth period, the average difference in the atomic weights of the successive members is 2·47; it begins with potassium, followed by calcium, scandium, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, and copper; after which come zinc, gallium, germanium, arsenic, selenium, bromine, and krypton, these last seven elements forming the natural homologues of the last seven elements of the third and fourth periods. In the sixth period, the average difference in the atomic weights of the successive members is 2·5, and of the eighteen elements required for this period seventeen are known, the missing member being the homologue of manganese. This period begins with rubidium and strontium and ends with iodine and xenon.

The seventh and eighth periods should, it is shown, consist of thirty-three elements each; and whilst, at present, only three elements of the eighth period are known, namely, radium, thorium, and uranium, the blank spaces in the seventh period are nine in number. The seventh period begins with cæsium, followed by barium, and between barium and tantalum room is found for the metals of the rare earths, from lanthanum to ytterbium, a position in accord with Benedick's [1] view

[1] *Zeit. anorg. Chem.*, 1904, **39**, 41.

													–	–
													–	He 4
								Be 9·1	B 11	C 12	N 14·04	O 16·00	Fl 19	Ne 20
								Mg 24·36	Al 27·1	Si 28·4	P 31·0	S 32·06	Cl 35·45	A 39·9
Ti 48·1	V 51·2	Cr 52·1	Mn 55·0	Fe 55·9	Co 59·0	Ni 58·7	Cu 63·6	Zn 65·4	Ga 70	Ge 72	As 75·0	Se 79·1	Br 79·96	Kr 81·12
Zr 90·7	Nb 94	Ma 96·0	–	Ru 101·7	Rh 103·0	Pd 106	Ag 107·93	Cd 112·4	Tn 114	Sn 118·5	Sb 120	Te 127·6	I 126·95	X 128
–	Ta 183	W 184·0	–	Os 191	Ir 193·0	Pt 194·8	Au 197·2	Hg 200·3	Tl 204·1	Pb 206·9	Bi 208·5	–	–	–
–	–	–	–	–	–	–	–	–	–	Pb a ?	Bi a ?	Te a ?	–	–

mentioned in last year's Report. The other members of this period are tantalum and tungsten, the homologues of niobium and molybdenum, osmium, iridium, platinum, and gold, which are placed in association with ruthenium, rhodium, palladium, and silver in the sixth period, and finally, mercury, thallium, lead, silver, and bismuth, which respectively find positions as members of groups II, III, IV, and V in the older tables of the elements.

The main features which distinguish Werner's mode of tabulation from that adopted by Mendeléeff are seen to be in the separation of the two sections of the elements of Group II from one another. Into this space are introduced the members of Group VIII, together with those elements of which the sub-groups are composed; in this manner also the elements of the rare earths fall quite naturally into position. Further, the nonvalent elements of the argon family are brought together into a group, between the strongly electro-negative elements, the halogens, and the electro-positive alkali metals. The blank spaces in the table indicate that additions to the elementary substances may be expected among the rare earths and in other parts of the seventh period, but it is chiefly in the eighth period that elements are lacking; these vacancies may possibly be supplied by such substances as radioactive tellurium, &c. Although it cannot be claimed that the arrangement under discussion obviates all the difficulties met with in a systematic arrangement of the elements in order of their atomic weights, still it may be fairly regarded as affording a clear exposition of the relations

between the properties of the elements and their atomic weights. Some of the difficulties experienced in arranging the elements in the order of their atomic weights are specially indicated in the foregoing table by the enclosure of certain of the elements with thick lines.

Revision of Atomic Weights.

Investigations dealing with the revision of the accepted atomic weights of some fourteen elements have been published during the year, and of these the most interesting is the method adopted by H. B. Dixon and E. C. Edgar [1] for the redetermination of the atomic weight of chlorine by the direct synthesis of hydrogen chloride. The chlorine employed was prepared by the electrolysis of fused silver chloride; it was liquefied and weighed in a sealed glass globe, from which it was allowed to evaporate into an exhausted combustion globe, in which the combination with hydrogen took place, the hydrogen chloride formed being absorbed by water in this combustion globe, cooled by melting ice. The hydrogen employed was produced by the electrolysis of a solution of barium hydroxide, and after drying was absorbed by metallic palladium in a weighed vessel. The hydrogen driven off by heat from the palladium was conveyed into the combustion globe, filled with chlorine, then ignited by a spark, and burnt at a jet. The gases were carefully regulated so as to maintain the hydrogen burning until nearly all the chlorine was used up; then the palladium was allowed to cool and the hydrogen turned off just before the flame died out. As already mentioned, the hydrogen chloride was absorbed by the water in the combustion globe, and the residual gas left in the globe was analysed, the chlorine being determined by breaking a thin glass bulb containing a solution of potassium iodide, the liberated iodine being estimated by titration with a solution of sodium thiosulphate. In each experiment, about 11 litres of each of the gases were consumed, the unused chlorine being about 2 per cent. of the volume burnt. The mean value obtained for the atomic weight of chlorine from nine of these experiments is 35·463 (O = 16), which is somewhat higher than either Stas's value (35·457) or that calculated by Clarke, namely, 35·447. In their revision of the atomic weights of sodium and chlorine, T. W. Richards and R. C. Wells [2] give results which indicate that the value 107·920 for the atomic weight of silver is more correct than 107·930. With the former of these values for silver then the atomic weight of sodium is 23·006, and for chlorine 35·470, whereas with the value 107·930 for silver the atomic weights of sodium and chlorine become 23·008 and 35·473 respectively.

[1] *Phil. Trans.*, 1905, Series *A*, **205**, 169.
[2] *J. Amer. Chem. Soc.*, 1905, **27**, 459.

The atomic weight of nitrogen has formed the subject of several communications; Hinrichs,[1] for example, has drawn attention to the fact that the results recently obtained [2] give values approaching nearly the true value, namely, 14·00. Gray,[3] from the determination of the density of nitric oxide, carefully purified by liquefaction and subsequent fractionation of the liquid, as also by the complete gravimetric analysis of this compound, has deduced the value 14·01 as the atomic weight of nitrogen. In a recent note, Scott [4] has drawn attention to the fact that by the titration of ammonium bromide against silver he had in 1901 arrived at the value 14·01 for the atomic weight of nitrogen, and that the discrepancy between the value obtained from the experiments made with ammonium chloride disappears if Richard's value, namely, 35·473, for the atomic weight of chlorine is used instead of the value 35·457. Using the former of these values, Scott's analysis of ammonium chloride gives 14·013 as the atomic weight of nitrogen.

From the analysis of the chloride, Richards [5] has obtained for strontium the value 87·661 as its atomic weight (Cl = 35·473), a value agreeing well with that deduced from the bromide, namely, 87·663. By the analysis of cadmium chloride, Baxter and Hines [6] obtain 112·469 for the atomic weight of the metal.

From the analysis of carefully purified silicon tetrachloride, Becker and Meyer [7] obtain as a mean of eight experiments the value 28·21 (O = 16) for the atomic weight of silicon.

Baxter [8] has again attacked the revision of the atomic weight of iodine by determining the ratio of silver iodide to silver chloride by converting the former first into silver bromide, then into the chloride. One series gave the atomic weight of iodine as 126·985, and a second series gave 126·984 (Cl = 35·473 and Ag = 107·93). A redetermination of the ratio of iodine to silver iodide has given results varying from 126·983 to 126·989. Köthner and Aeuer [9] have also discussed this subject and deduced from the forty-one determinations made by Scott, Ladenburg, Baxter, and themselves a value 126·97 (O = 16).

A special interest attaches to the atomic weight of tellurium, by reason of its position in the natural system of the elements, and on this subject are two publications; in one is given the result of the determination of the electro-chemical equivalent of this element, from which the atomic weight 127·61 is deduced (Ag = 107·93).[10] In the second, from the reduction of tellurium dioxide by hydrogen and by

[1] *Compt. rend.*, 1905, **140**, 1590.
[2] See *Ann. Reports*, 1904.
[3] *Trans.*, 1905, **87**, 1601.
[4] *Proc.*, 1905, **21**, 309.
[5] *Zeit. anorg. Chem.*, 1905, **47**, 145.
[6] *J. Amer. Chem. Soc.*, 1905, **27**, 222.
[7] *Zeit. anorg. Chem.*, 1905, **43**, 251.
[8] *J. Amer. Chem. Soc.*, 1905, **27**, 876.
[9] *Annalen*, 1904, **337**, 362.
[10] G. Gallo, *Atti R. Accad. Lincei*, 1905, [v], **14**, 1, 23, and 104.

hydrazine Gutbier [1] obtained for the atomic weight of tellurium the value 127·6. In a paper dealing with the chemical properties and combining weight of palladium, Amberg [2] has described a trustworthy method for estimating the chlorine in palladium chloride, and also a method of precipitating the metal electrolytically from solution of its sulphate. The new electrolytic process has given as the mean of several results 106·7 for the atomic weight of palladium. Parsons [3] has calculated values for the atomic weights of glucinum and of carbon from the results of the determination of the equivalent weight of glucinum by analysis of the acetylacetonate and basic acetate. These calculations give for glucinum the value 9·112 and for carbon 12·007. Parsons [4] has also criticised Pollok's conclusion, mentioned in last year's Report, that the beryl from Limoges contains an element of high atomic weight associated with glucinum, a conclusion from which he dissents mainly on the grounds that the low proportion of chlorine noted by Pollok in the separate fractions of chloride may have been due to the action of moisture on the glucinum chloride, which would entail a loss of chlorine.

Atomic Weights and Specific Heats.

The law of Dulong and Petit and Neumann's extension formed the subject of the presidential address to the Society,[5] in which Tilden has given a summary of our present knowledge of "the relation of specific heat to atomic weight in elements and compounds." Many additional data to those already published are given, and it is shown that influence of temperature on specific heat is greater than hitherto supposed. Further, as there are no conditions under which the law of Dulong and Petit is true of all elements, the mean specific heat of metals between 0° and 100° may be taken as the nearest approach to a constant available for practical purposes, the elements of low atomic weight being regarded as exceptions. It is also pointed out that the atomic heats of elements in the gaseous state may possibly be equal. Experimental results give for hydrogen 2·4, for oxygen 2·5—2·7, and 2·6 for carbon in carbon dioxide.

Rare Elements.

The anhydrous chlorides of lanthanum, neodymium, praseodymium, samarium, and yttrium have been prepared by Matignon [6] by the action of vapours of sulphur chloride, chlorine, and hydrogen chloride on the

[1] *Annalen*, 1905, **342**, 266.
[2] *Ibid.*, **341**, 235.
[3] *J. Amer. Chem. Soc.*, 1905, **27**, 1204; also *Zeit. anorg. Chem.*, 1905, **46**, 215.
[4] *J. Amer. Chem. Soc.*, 1905, **27**, 233.
[5] *Trans.*, 1905, **87**, 551.
[6] *Compt. rend.*, 1905, **40**, 1181.

residues left by evaporation of the metallic oxides with hydrochloric acid. The heats of formation of the chlorides of the first four of these elements, when produced by the dissolution of their oxides in hydrochloric acid, are given as 80·3, 73·9, 71·6, and 34·2 cals. respectively.[1] Anhydrous neodymium chloride has been thoroughly investigated by Matignon.[2] It is a stable compound not attacked by hydrogen at 1000°, but is converted by oxygen into the oxychloride NdOCl, which forms mauve-tinted plates, infusible at 1000°. From the chloride, the iodide (NdI_3) and bromide ($NdBr_3$) have been obtained by the action of the corresponding hydracids. The chloride is not attacked by ammonia at the ordinary temperature, but when heated with it forms additive compounds. Heated with acetylene, the chloride is unaltered, the acetylene polymerises, and carbon is deposited in a form possessing brilliant reflecting surfaces, which is not graphite. The probable existence of an oxide, Nd_4O_7, is maintained by Waegner.[3] Matignon and Trannoy[4] describe a series of eight compounds which ammonia forms with anhydrous samarium chloride, of which the formulæ and temperatures of dissociation are given. By the application of the Demarçay-Drossbach method of separation, Feit and Przibylla[5] have obtained neodymium, samarium, and lanthanum from monazite earths, from which source also Feit[6] has obtained preparations of terbium, for which element the atomic weight 158·6 is deduced. Urbain[7] has by careful fractionation obtained 7 grams of the oxide of the element Z_δ, to which he is of the opinion the name terbium should be restricted. The oxide exhibits an absorption band $\lambda = 488$, and the solutions of its chloride give the beautiful green fluorescent spectrum of Lecoq de Boisbaudran's Z_β. The oxide when pure is non-fluorescent, but when mixed with gadolinia or with alumina it then exhibits fluorescence. The value deduced for the atomic weight is 159·2 (O = 16). The oxide is black or brown, according as it is prepared from the oxalate or sulphate; its salts are colourless and slightly more soluble than those of gadolinium.

It would appear that much remains to be done to clear up matters relating to gadolinium and the elementary substances associated with it. Urbain[8] has succeeded in obtaining pure compounds of this element from gadolinium earths by crystallisation of the double nitrate of gadolinium and nickel, and from the conversion of the sulphate, $Gd_2(SO_4)_3 + 8H_2O$, into the oxide, (Gd_2O_3), deduced the atomic weight of 157·23—157·25 for this metal. Crookes, from observations of the ultra-

[1] *Compt. rend.*, 1905, **40**, 1339.
[2] *Ibid.*, 1637.
[3] *Zeit. anorg. Chem.*, 1904, **42**, 118.
[4] *Compt. rend.*, 1905, **140**, 140.
[5] *Zeit. anorg. Chem.*, 1905, **43**, 202.
[6] *Ibid.*, 267.
[7] *Compt. rend.*, 1904, **139**, 736; 1905, **141**, 521.
[8] *Ibid.*, 1905, **140**, 583.

violet spectrum of gadolinium purified by the Urbain-Lacombe method [1] (see Ann. Report, 1904), has concluded that victorium is present as an impurity in the gadolinium. According to the same authority,[2] the oxide of europium, prepared by the same method, gives an ultra-violet spectrum indicating the presence in it of gadolinium, yttrium, lanthanum, and calcium, whereas Eberhard's [3] spectrographic investigation of the Urbain-Lacombe method for the separation of samarium, europium, and gadolinium shows the method to be satisfactory as a means of obtaining pure europium salts, also samarium free from europium, and gadolinium free from samarium. Gadolinium, according to Urbain,[4] whether obtained from monazite, xenotine, or pitchblende, exhibits certain new lines in the ultra-violet absorption spectrum. Further, the metal shows the same phosphorescent spectrum as that attributed by Crookes to victorium, which Urbain does not consider to have been definitely shown to be different from gadolinium.

The high values of the heat of formation of the oxides of the cerite metals indicate that the metals should prove powerful reducing agents. This indication has been verified by Weiss and Aichel,[5] who, by the aid of the "mixed metals" obtained from the residual oxides in preparing thorium nitrate, have reduced many metallic oxides to the metallic state. In this way, the following metals have been produced: iron, nickel, cobalt, manganese, chromium, molybdenum, vanadium, tantalum, niobium, tungsten, uranium, and columbium.

Wolff,[6] in detailing the results of the determination of the solubilities of double nitrates and double sulphates of cerium and ammonium, has described the composition and properties of several cerous salts of the fatty acids. Cerous trichloracetate, $Ce(C_2Cl_3O_2)_3,3H_2O$, is distinguished from the others by the fact that when its aqueous solution is boiled the cerium separates out as carbonate and that the salt is not oxidised by hydrogen peroxide.

Meyer and Gumperz [7] are unable to confirm Baskerville's observations on the composite nature of thorium (see Ann. Report, 1904), and their conclusions are supported by Eberhard's [8] spectrographical investigations of thorium preparations from various sources. Baskerville and Zerban [9] have discovered a new source of thorium in a rock from South America, which consists chiefly of barium carbonate with a little inactive thoria. An analysis of thorianite, the only British source of thoria, found in Ceylon, has been recently published by Dunstan and Blake.[10] This mineral contains some 70 per cent. of thoria, and is possibly isomorphous

[1] *Proc. Roy. Soc.*, 1905, Series *A*, **74**, 420.
[2] *Ibid.*, 550.
[3] *Zeit. anorg. Chem.*, 1905, **45**, 374.
[4] *Compt. rend.*, 1905, **140**, 1233.
[5] *Annalen*, 1905, **337**, 370.
[6] *Zeit. anorg. Chem.*, 1905, **45**, 89.
[7] *Ber.*, 1905, **38**, 817.
[8] *Ibid.*, 826.
[9] *J. Amer. Chem. Soc.*, 1904, **26**, 1642.
[10] *Proc. Roy. Soc.*, 1905, **76**, 253.

with uraninite; in addition to uranium, it contains the oxides of cerium, lanthanum, didymium, and yttrium, also zirconia and silica. Helium was found in one specimen of this mineral; the thorium is radioactive; inactive thorium is, according to Zerban [1] found in those minerals which do not contain uranium.

The reduction of thorium oxide when heated in an electric furnace with amorphous boron has been studied by Jassonneix [2] and by E. Wedekind and Fetzer.[3] The first of these authorities obtained two borides, namely, the compound ThB_4, as a yellow, metallic powder, easily attacked by acids, and the substance ThB_6, a reddish-violet, amorphous substance not so readily acted on by acids. Thorium oxide is also reduced by silicon.

During the year, the following observations have been made on zirconium and its compounds; zirconia is not reduced when heated with metallic aluminium, and when heated with magnesium in a loosely covered crucible the nitride Zr_2N_3 is formed, together with a substance which forms a blue colloidal solution. The nitride is easily oxidised when heated in the air; it resists the action of alkalis and of acids, but is readily converted into chloride or bromide by the action of these halogens (Wedekind).[4] Stähler and Denk [5] describe the compounds which the zirconium halides form with gaseous ammonia. The iodide forms with liquid ammonia the compound $ZrI_4,8NH_3$, from which liquid ammonia removes ammonium iodide, indicative of the following decomposition: $ZrI_4,8NH_3 = Zr(NH_2)_4 + 4NH_4$. The following substances, $ZrI_4,6NH_2Et$ and $ZrI_4,4Et_2O$, have also been obtained. Compounds of the type R_2,H_2ZrCl_6 are, according to Rosenheim and Frank,[6] formed when alcoholic solutions of zirconium chloride are treated with the hydrochlorides of pyridine or quinoline. The authors also describe the complex sulphates $Zr_2O_3(SO_4K)_2,8H_2O$; $Zr_2O_3(SO_4Rb)_2,15H_2O$; $Zr_2O_3(SO_4Cs)_2,11H_2O$ and $Zr(SO_4K)_4,3H_2O$. From the fact that the normal zirconium sulphate does not exhibit reactions similar to those of the chloride, Ruer [7] concludes that it is a dibasic acid having the formula $ZrOSO_4,SO_4H_2$, forming salts of the type $ZrOSO_4,SO_4Ni_2$, and that the crystalline sulphate is to be represented by the formula $ZrOSO_4,SO_4H_2,3H_2O$ and not $Zr(SO_4)_4,4H_2O$. Ruer [8] has also specially studied the hydrolysis of zirconium oxychloride and obtained a hydroxide, metazirconic acid, which is related to the ordinary hydroxide as metastannic acid is to stannic acid. It is suggested by van Bemmelen [9] that

[1] *Ber.*, 1905, **38**, 557.
[2] *Compt. rend.*, 1905, **141**, 191.
[3] *Chem. Zeit.*, 1905, **29**, 1031.
[4] *Zeit. anorg. Chem.*, 1905, **45**, 385.
[5] *Ber.*, 1905, **38**, 2011.
[6] *Ibid.*, 812.
[7] *Zeit. anorg. Chem.*, 1904, **42**, 87.
[8] *Ibid.*, 1905, **43**, 282.
[9] *Ibid.*, **45**, 83.

the proportion of water in metazirconic acid observed by Ruer is accidental.

Considerable interest surrounds the production of tantalum, already referred to, a description of which has been given by von Bolton.[1] A very complete account is given of the physical constants of this metal, which combines extraordinary hardness with great ductility; the metal melts about 2250°. Tantalum in the form of wire is used for the construction of incandescent electric lamps; the red-hot metal decomposes water, combines with sulphur, selenium, and tellurium, and forms alloys with iron, molybdenum, and tungsten, but not with silver. The fact that when heated at a white heat it does not combine with oxygen if the pressure be below 20 mm. gives a clue to the explanation of the method of preparing the metal, which is effected by heating electrically in a vacuum rods made of the compressed oxides. At the high temperature so attained, the oxide is decomposed and the oxygen removed by continued exhaustion. It has also been pointed out by von Bolton[2] that the hardness of the metal tantalum is largely increased by the presence of its oxide. Von Pirani[3] has also shown that this metal absorbs a considerable volume of hydrogen when heated in this gas, and that the hydride is formed when the pentachloride and hydrogen are passed through a heated tube.

Vanadium and columbium may also be obtained in a similar manner from their oxides, which in the form of compressed powder conduct electricity. Columbium is more ductile than vanadium and melts at 1950°, whilst the latter melts at 1680°. Goldschmidt's process has been utilised in the production of metallic vanadium, yielding a product containing 78·2—81·1 per cent. of the element.[4] This crude metal, treated with chlorine, yields a mixture of VCl_4 and $VOCl_3$, which can be separated by fractional distillation. Koppel and Kaufmann also describe a compound of vanadium oxychloride and pyridine,

$$VOCl_3,C_5NH_5HCl,C_2H_6O,$$

formed by the interaction of pyridine and an alcoholic solution of the oxychloride. They were not successful in obtaining the thiochloride, $VSCl_3$, but by heating vanadium sulphide, V_2S_3, in chlorine the compound $4VSCl_3,S_2Cl_2$ is produced, from the ethereal solutions of which brown tablets of the composition $4VSCl_3,S_2Cl_2,C_4H_{10}O$ separate. Vanadium oxychloride is formed when the pentoxide suspended in ether, acetic acid, or alcohol is treated with gaseous hydrogen chloride, the temperature being kept low to prevent the production of vanadyl chloride, $VOCl_2$. With the hydrochlorides of pyridine and of quinoline, vanadyl chloride forms two series of double salts; one series,

$$VOCl_2,4(RHCl),xH_2O,$$

[1] *Zeit. Elektrochem.*, 1905, **11**, 45. [2] *Ibid.*, 503. [3] *Ibid.*, 555.
[4] *Zeit. anorg. Chem.*, 1905, **45**, 352.

green in colour, and another series, $VOCl_2,2(RHCl),xH_2O$, the members of which are blue.[1] The first of these is produced with solvents such as absolute alcohol, glacial acetic acid, or a mixture of alcohol and ether, which show but little ionisation, whereas the addition of water to these solvents results in the production of the blue compounds. Similar changes in colour are observed on the addition of water to the solutions of vanadyl chloride in alcohol or glacial acetic acid.

An instance of the passage of a compound from a higher into a lower state of oxidation has been observed by Prandtl,[2] who found that when a mixture of vanadium pentoxide and sodium carbonate to which some phosphoric acid has been added is fused before the blowpipe and allowed to cool slowly, the mass gave off oxygen. Prandtl and Lustig,[3] by dissolving vanadium pentoxide in aqueous solutions of selenious acid, have obtained vanadioselenious acid, $3V_2O_5,4SeO_2,H_2O_4$, from which, by treatment with alkalis, a red and a yellow series of vanadioselenites are obtained. Gold is dissolved by vanadic acid in presence of hydrochloric acid, and from these solutions it is precipitated as a greyish-violet powder on treatment with an alkali. The following reaction is, therefore, reversible under the conditions mentioned :

$$3VOCl_3 + Au \underset{\text{Alkaline.}}{\overset{\text{Acid.}}{\rightleftarrows}} 3VOCl_2 + AuCl_3.$$

Selenic and telluric acids behave in a similar manner, and on this reaction Hundeshagen[4] has based a method of testing minerals for vanadium.

The Argon Group.

Depending on the different behaviour of these gases when brought into contact with charcoal cooled by liquid air, a method of separating neon, krypton, and xenon has been described by Valentiner and Schmidt,[5] whilst Ramsay[6] has utilised the same property to determine the proportion of neon and helium in the atmosphere, with the following results : neon, 0·0000086 per cent. by weight and 0·0000123 by volume ; helium, 0·00000056 per cent. by weight and 0·000004 by volume ; the percentage of argon is given as 0·937.

An appliance for grinding solids in a vacuum has been devised by Moss,[7] who has applied the same to the study of the gases given off from pitchblende and the condition in which helium exists in this mineral.

[1] *Zeit anorg. Chem.*, 1905, **45**, 345.
[2] *Ber.*, 1905, **38**, 657.
[3] *Ibid.*, 1305.
[4] *Chem. Zeit.*, 1905, **29**, 799.
[5] *Sitzungsber. K. Akad. wiss. Berlin*, 1905, **38**, 816.
[6] *Proc. Roy. Soc.*, 1905, Series *A*, **76**, 111.
[7] *Roy. Dub. Soc. Trans.*, 1905, **8**, 153.

Many of the investigations and the results obtained may conveniently be classified under the headings of the several groups in the periodic system of the elements. Judging by the number of communications published, the elements and compounds of Groups IV, V, VI, and VIII appear to have attracted special attention during the year.

Group I.

A.—The study of the action of sodamide on a number and variety of inorganic substances has shown this compound to be very energetic in its chemical properties, reducing the oxides of several metals and also certain metallic chlorides to the metals. With some oxy-compounds, such as nitrates of lead and silver, deflagration takes place when sodamide is rubbed with them, whilst when heated with potassium chlorate it explodes with considerable violence (Ephraim).[1]

Loeb[2] has noted a difference between sodium and potassium iodides; when crystallised from alcoholic solutions, the latter crystallises without any of the solvent, whereas the sodium iodide separates in the form of compounds with the solvent; in this manner the following have been obtained: $NaI,3CH_3\cdot OH$; $NaI,C_2H_5\cdot OH$, and $5NaI,3C_3H_7\cdot OH$.

By the action of sodium polysulphide in presence of caustic soda on sodium hyposulphite,[3] both sodium sulphite and sulphate are formed, possibly with the temporary production of a thiosulphite, thus:

(1) $Na_2S_2O_4 + Na_2S_2 + 2NaOH = Na_2S_2O_2 + Na_2SO_3 + Na_2S + H_2O$.
(2) $Na_2S_2O_2 + 2NaOH = Na_2S + Na_2SO_3 + H_2O$.

A study of the crystalline forms of potassium and thallous salts[4] has revealed the isomorphism of the perchlorates, neutral sulphates, acid sulphates, and other oxy-salts of these metals.

From the determination of the solubility of bromine in solution of potassium bromide, Worley[5] has adduced evidence in support of the existence of the tribromide, KBr_3.

Metallic rubidium and cæsium[6] can be obtained by heating the fused chlorides with calcium in exhausted glass tubes; the reaction commences at 400—500° and the heat of the reaction is sufficient to volatilise the metals. The pentasulphides of these metals are formed when the monosulphides are warmed with sulphur and an aqueous alkali hydroxide in an atmosphere of hydrogen; Rb_2S_5 crystallises in red prisms melting at 223—224°; Cs_2S_5,H_2O forms red crystals melting at 202°.[7] The fluoride and double fluorides of rubidium are described by Eggeling and Meyer.[8]

[1] *Zeit. anorg. Chem.*, 1905, **44**, 185.
[2] *J. Amer. Chem. Soc.*, 1905, **27**, 1019.
[3] Binz, *Ber.*, 1905, **38**, 2051.
[4] *Rec. trav. chim.*, 1905, **24**, 65.
[5] *Trans.*, 1905, **87**, 1107.
[6] Hackspill, *Compt. rend.*, 1905, **141**, 101.
[7] *Ber.*, 1905, **38**, 123.
[8] *Zeit. anorg. Chem.*, 1905, **46**, 174.

Rengade[1] has described the production of cæsamide, ($CsNH_2$), by the spontaneous decomposition of cæsium-ammonium, a reaction which is complete at 120°. From liquid ammonia, the amide separates as a white, crystalline solid; it is readily oxidised, forming ammonia, and cæsium nitrite and hydroxide. Potassamide behaves in a similar manner, whereas sodamide is not oxidised. The oxidation of cæsium-ammonium in liquid ammonia, under different conditions of temperature, yields the oxides Cs_2O_2, Cs_2O_3, and Cs_2O_4. By the slow oxidation of cæsium-ammonium, the hydroxide and amide are formed; when the mixture is heated, the monoxide and amide react, producing cæsium hydroxide, metallic cæsium, and nitrogen.

B.—Naumann and Rücker[2] conclude that the solubility of silver nitrite is influenced by silver nitrate, much as sodium acetate affects the solubility of silver acetate, a conclusion adversely criticised by Abegg and Pick,[3] who find that only a portion of the silver nitrite is ionised.

Clarke,[4] by heating finely-divided minerals mixed with silver or thallous nitrate in sealed tubes at the melting point of these nitrates, has shown that the sodium in silicates like analcite may be replaced by silver or thallium; thus, from $NaAlSi_2O_6,H_2O$ both $AgAlSi_2O_6,H_2O$ and $TlAlSi_2O_6$ have been prepared.

Aurous iodide,[5] AuI, is formed when iodine acts on gold at temperatures ranging from 50° to the melting point of iodine; it is a green solid and can only be freed from excess of iodine by volatilising the latter at 30°. When heated to a somewhat higher temperature, it forms yellow plates, and at 190° is resolved into its constituent elements.

The production of a red hydrosol of gold[6] by the action of carbon monoxide on dilute solutions of gold chloride (0·002—0·05 per cent. of gold) may be used as a means of detecting small quantities of carbon monoxide mixed with air.

The melting point of gold is given as 1066·1—1067·4° by Jaquerod and Perrot[7] from determinations made with thermometers constructed of silica and filled with different gases, namely, nitrogen, air, carbon dioxide, carbon monoxide, and oxygen. The authors find that neither hydrogen nor helium can be used in these thermometers, as these gases diffuse through the silica, the diffusion commencing at 200° with hydrogen, and possibly below 100° with helium. Results obtained with porcelain thermometers filled with nitrogen are also vitiated by diffusion of the gas. A process for the extraction of gold from sea water is described by de Wilde.[8] Van Heteren[9] concludes that the allotropism of gold has not been satisfactorily demonstrated.

[1] *Compt. rend.*, 1905, **140**, 1183 and 1536.
[2] *Ber.*, 1905, **38**, 2292.
[3] *Ibid.*, 2571.
[4] *Zeit. anorg. Chem.*, 1905, **46**, 191.
[5] *Compt. rend.*, 1904, **139**, 733.
[6] Donau, *Monatsh.*, 1905, **26**, 525.
[7] *Arch. Sci. phys. nat.*, 1905, **20**, 128.
[8] *Ibid.*, [iv], **19**, 559.
[9] *Chem. Centr.*, 1905, **1**, 503.

Many investigations have been made of the phenomena associated with the alloying of different metals with copper, silver, and gold, in many instances the fusion diagrams indicating the formation of definite compounds of the metals concerned.

Gutbier and Hofmeier [1] obtain various coloured hydrosols of silver by the reduction of silver nitrate solutions containing gum arabic with hydrazine sulphate. Ammoniacal solutions of phenylhydrazine and hypophosphorous acid may also be used to reduce silver nitrate. In the electro-deposition of silver from solutions of the nitrate, good coherent deposits are obtained if the cathode is rotated and the cathodic and anodic liquids separated; further, by the addition of glue to the solutions, smooth, bright, purple or yellow deposits are obtained resembling the deposits obtained by Carey-Lea from solutions of organic salts (Snowdon [2]).

Group II.

A.—Some of the physical constants of metallic calcium have been determined by Moissan and Chavanne,[3] who describe an amalgam, $CaHg_8$, formed by dissolving the metal in mercury; it is stable in dry air, is slowly attacked by water, and is useful as a reducing agent. Arndt [4] has prepared three distinct alloys of calcium and aluminium, containing 23·4, 41·74—45·44, and 80·55—83·32 per cent. of calcium respectively. From these alloys, containing a large proportion of aluminium, the calcium can be separated by distillation under reduced pressure. Alloys are also produced by electrolysing fused calcium chloride, using aluminium as cathode. For the purification and sterilisation of drinking water, the use of calcium peroxide has been suggested; 0·4 gram sterilises a litre in from fifteen to twenty minutes.[5] Monocalcium silicate in the form of hexagonal crystals has been prepared by Benzian [6] by heating sand and chalk together in a graphite crucible.

Laboratory methods for preparing calcium by the electrolysis of the fused chloride are described by Wöhler [7] and by Goodwin.[8]

Strontium-ammonium is formed in reddish-brown crystals by the action on strontium of dry ammonia at 60°.[9] Barium amide, $Ba(NH_2)_2$,[10] is produced by the action of potassammonium on barium bromide; the last-named compound forms with dry ammonia the compound $BaBr_2,8NH_3$.

The phosphorescence of barium sulphide, prepared by the ignition of the thiosulphate, is much intensified by the addition of the nitrates of

[1] *Zeit. anorg. Chem.*, 1905, **45**, 77.
[2] *J. Physical Chem.*, 1905, **9**, 392.
[3] *Compt. rend.*, 1905, **140**, 122.
[4] *Ber.*, 1905, **38**, 1472.
[5] Freyssingi and Roche, *Rev. intern. Falsif.*, 1905, **18**, 49.
[6] *Chem. Zeit.*, 1905, **29**, 737.
[7] *Zeit. Elektrochem.*, 1905, **11**, 612.
[8] *J. Amer. Chem. Soc.*, 1905, **27**, 1403.
[9] *Compt. rend.*, 1905, **140**, 1252.
[10] *Ibid.*, 1243.

uranium, bismuth, or thorium before ignition; these substances exert a like influence on strontium sulphide.[1] The precipitation of calcium carbonate from solutions of the nitrate by alkali carbonates has been thoroughly examined by Meigen,[2] who has also determined the conditions of the change from amorphous carbonate to aragonite and calcite. A study of the influence of temperature and concentration of solutions of ammonium, potassium, and sodium chlorides on the action of these substances on the carbonates of the alkaline earths has shown the rate of action of the chlorides to be in the order named, whereas the following is the order in which the carbonates resist the action of the chlorides: barium, calcium, strontium; common salt has no action on strontium carbonate.[3]

B.—Many examples of the reducing action of magnesium in form of ribbon and powder are described by Faktor,[4] amongst others the reduction of solutions of magenta, benzoquinone, potassium ferricyanide, and indigo. Carrick Anderson[5] has found the basic carbonates of magnesium to be more complex than is usually supposed, the samples examined by him corresponding to the formulæ

$$20MgCO_3;\ 21Mg(OH)_2,6H_2O;$$

$14MgCO_3,10Mg(OH)_2,75H_2O$; and $19MgCO_3,20Mg(OH)_2,65H_2O$. All are decomposed completely to the oxide when heated in an open vessel, but at temperatures ranging from 750° to 810°; the higher the temperature at which the oxide is formed the more slowly does it dissolve in water. According to Brill,[6] the temperature at which the products of dissociation exert a pressure of one atmosphere is in the case of calcium carbonate 825°, and 1155° for strontium carbonate. Magnesium carbonate forms a series of basic carbonates, the temperatures of dissociation of seven of which are given.

Grube,[7] from an examination of the alloys of magnesium and lead concludes that one compound, $PbMg_2$, is formed, similarly tin forms only one definite compound, $SnMg_2$, conclusions which are confirmed by Kurnakoff and Stepanoff.[8] With thallium there are indications of the existence of the three following compounds: Tl_3Mg_8, $TlMg_3$, and Tl_2Mg_3.[9] Magnesium and aluminium[10] appear to form only one definite compound, Al_3Mg_4, in the form of very brittle, silver-white needles. The alloys containing from 5 to 30 per cent. of magnesium are technically known as magnalium. A second series of alloys form homogeneous conglomerates of mixed crystals, capable of a high polish, whilst those containing 55 to 68 per cent. of magnesium consist of the crystals

[1] Vanino and Gaus, *J. pr. Chem.*, 1905, [ii], **71**, 196.
[2] *Chem. Centr.*, 1905, [i], 1363.
[3] *Bull. Soc. chim.*, 1905, [iii], **33**, 13.
[4] *Chem. Centr.*, 1905, [i], 1305.
[5] *Trans.*, 1905, **87**, 257.
[6] *Zeit. anorg. Chem.*, 1905, **45**, 275.
[7] *Zeit. anorg. Chem.*, 1905, **44**, 117.
[8] *Ibid.*, **46**, 177.
[9] *Ibid.*, **46**, 76.
[10] *Ibid.*, **45**, 225.

of Al_3Mg_4 mixed with a soft eutectic. The alloys of magnesium and aluminium together with other alloys containing the latter metal, when recently filed, decompose water with the liberation of hydrogen, the oxygen being absorbed by the aluminium (Pecheux).[1]

Both mercurous and mercuric thiocyanates dissolve in potassium thiocyanate, forming complex double salts.[2] Ditte[3] has obtained a series of double salts by the action of concentrated sulphuric acid and of mercury sulphate in sulphuric acid on mercuric iodide. When mercuric oxide is heated with mercurous halides in sealed tubes at 160—180°, the following oxyhalides are formed: HgCl,HgO; HgBr,HgO; and HgI,3HgO;[4] they are red solids. The preparation of a series of heavy liquids by adding alternately mercuric iodide and an alkali iodide to water until saturated is described by Duboin.[5] The specific gravities of the liquids range from 2·98, that of the ammonium mercuric iodide, to 3·46, the specific gravity of the sodium mercuric iodide.

The amount of the precipitate formed when a solution of ammonium mercuric chloride is added to a natural water is proportional to the temporary hardness; no precipitate is formed if the water has been previously boiled.[6]

Group III.

A.—Perborates are described by Jaubert,[7] also by Bruhat and Dubois.[8] According to the first author the perborate, $Na_2B_4O_8,10H_2O$, is obtained by adding boric acid and sodium peroxide to water; by treatment of this compound with hydrochloric acid equivalent to half the sodium contained in it, crystals of the perborate, $NaBO_3,4H_2O$, separate out. Bruhat and Dubois obtain this compound by the electrolysis of solutions of sodium orthoborates. The perborates are stable in the solid state, but their solutions on warming readily decompose with the liberation of oxygen. The solutions of the perborates contain hydrogen peroxide and provide a good method of preparing this substance.[9]

A complex series of calcium chloroborates formed by fusing boron trioxide and calcium chloride together is described by Ouvrard.[10] Wedekind and Fetzer[11] have obtained two manganese borides; the boride MnB_2 is formed by heating boron with manganese thermite,

[1] *Compt. rend.*, 1905, **140**, 1535.
[2] Grossmann, *Zeit. anorg. Chem.*, 1905, **43**, 356.
[3] *Compt. rend.*, 1905, **140**, 1162.
[4] Fischer and von Wartenberg, *Chem. Zeit.*, 1905, **29**, 308.
[5] *Compt. rend.*, 1905, **141**, 385.
[6] Villenet and Chenu, *Bull. Soc. chim.*, 1905, [iii], **33**, 944.
[7] *Compt. rend.*, 1904, **139**, 711.
[8] *Ibid.*, 1905, **140**, 506.
[9] *Chem. Centr.*, 1905, [ii], 99.
[10] *Compt. rend.*, 1905, **141**, 351.
[11] *Ber.*, 1905, **38**, 1228.

whilst MnB is produced by heating manganese suboxide with boron in the electric furnace.

B.—The double chromium aluminium silicide, Cr_2AlSi_3, and also the compound Cr_2AlSi_4, are formed by heating together chromium, potassium dichromate, or potassium chromofluoride with a large excess of potassium silicofluoride and aluminium. They are dark grey, crystalline solids, which resist the action of acids excepting hydrofluoric acid, and are attacked by molten alkali hydroxides. Similar tungsten compounds have been prepared.[1]

The solution of aluminium chloride in carbonyl chloride leaves on evaporation the compound $2AlCl_3,5COCl_2$, from which, by the gradual removal of carbonyl chloride, other compounds are produced, until finally the double chloride, $AlCl_3,COCl_2$, is formed, which forms silky needles and is not decomposed at 750°. This compound is present in commercial aluminium chloride and is formed when aluminium chloride is distilled in carbonyl chloride or when carbon monoxide and aluminium chloride are together passed through red-hot tubes.[2]

Colani[3] has described the production of phosphides, arsenides, antimonides, silicides, and borides of metals by heating a mixture of a metallic oxide with the non-metal or its oxide and aluminium powder. The mixture is inflamed by a magnesium cartridge; in case infusible products are expected to result from the action, the addition of copper oxide or tin oxide should be made to the aluminium. These observations are confirmed by Matignon and Trannoy.[4]

Pring,[5] in an investigation of the action of aluminium carbide, has found that up to 1400° the carbide acts as a reducing agent on metallic oxides, both constituents being oxidised, thus:

$$Al_4C_3 + 12MO = 2Al_2O_3 + 3CO_2 + 12M,$$

whereas at higher temperatures alloys of aluminium and the metal are produced and the carbon only oxidised, for example:

$$3CuO + Al_4C_3 = 4Al,3Cu + 3CO.$$

These results are explained by the fact that alumina can be reduced by carbon at high temperatures, whereas at low temperatures carbon monoxide oxidises aluminium. The reaction at low temperatures,

$$6Al + 3CO = Al_4C_3 + Al_2O_3,$$

is reversed at higher temperatures.

From the manner in which aluminium powder absorbs oxygen at

[1] Manchot and Kieser, *Annalen*, 1904, **337**, 353.
[2] Baud, *Compt. rend.*, 1905, **140**, 1688.
[3] *Ibid.*, **141**, 33.
[4] *Compt. rend.*, 1905, **141**, 190.
[5] *Trans.*, 1905, **87**, 1530.

different temperatures, Kohn-Abrest[1] infers the existence of several oxides of aluminium. Shepherd[2] has, by the study of the curves of the specific volumes of the alloys of zinc and aluminium, confirmed the conclusions of Heycock and Neville as to the non-existence of definite compounds of these metals. The effect of tempering on the copper aluminium bronze, known as "fortior," is similar to that produced on steel. The change is due to the production at 650—750° of a new constituent which appears in the form of needles embedded in a granular substance. This substance increases in quantity until at 950° it is the only constituent, the change being associated with a doubling of the elastic limit and breaking strain of the alloy. The composition of commercial varieties of magnalium and other light alloys which have been applied industrially has been dealt with by Barnett.[3]

Group IV.

A.—Moissan,[4] in repeating his experiments on the production of the diamond, has found that the yield is much increased by the presence of iron sulphide and of silicon. The same author has shown that the carbon silicide of the Cañon Diablo meteorite is identical with the synthetical silicide, CSi.[5] The heat of combustion of the carbon produced by the decomposition of acetylene is found by Mixter[6] to be 7894 cals., whereas those of sugar charcoal and graphite are 8057 and 7831 respectively. This carbon is regarded as another allotropic form of the element.

Ammonium cyanate and not cyanide is, according to Jackson and Laurie,[7] formed by the passage of a mixture of carbon monoxide and ammonia over heated platinum or by subjecting the mixture to silent electric discharge or by sparking the gases.

The proportion of incompletely oxidised carbon compounds in free air has been determined by Wolpert;[8] the proportion in the air of Berlin is given as 0·015 volume per 1000 volumes.

The action of carbon monoxide on dry silver oxide takes place at the ordinary temperature and is associated with an evolution of heat, thus:

$$Ag_2O + CO = Ag_2 + CO_2 + 61{\cdot}2 \text{ cals.}$$

In some instances it is necessary to apply heat to start this reaction, a temperature between 40° and 50° being sufficient. Silver oxide suspended in water reacts similarly, but better when dissolved in ammonia.[9]

[1] *Compt. rend.*, 1905, **141**, 323.
[2] *J. Physical Chem.*, 1905, **9**, 504.
[3] *J. Soc. Chem. Ind.*, 1905, **24**, 832.
[4] *Compt. rend.*, 1905, **140**, 277.
[5] *Ibid.*, 405.
[6] *Amer. J. Sci.*, 1905, **14**, 434.
[7] *Trans.*, 1905, **87**, 433.
[8] *Arch. Hygiene*, 1905, **52**, 151.
[9] Dejust, *Compt. rend.*, 1905, **140**, 1250.

The knowledge of titanium compounds has been greatly extended by the researches of Stähler [1] and of Stähler and Wirthwein.[2] As a means of producing the tetrachloride, rutile or titanic iron ore is converted into the carbide in the electric furnace, and the crude chloride formed from it by the action of chlorine; after shaking up with sodium amalgam, the product is distilled under reduced pressure. By the action of dry ammonia under different conditions, the compounds $TiCl_4,8NH_3$ and $TiCl_4,6NH_3$ are formed, from either of which, on treatment with liquid ammonia, titanamide, $Ti(NH_2)_4$, is obtained. Amongst the tervalent titanium compounds described is a series of sparingly soluble oxalates having the following formulæ: $Ti(C_2O_4)_3,10H_2O$; $Ti(NH_4)(C_2O_4)_2,2H_2O$; $TiK(C_2O_4)_2,2H_2O$; and $TiRb(C_2O_4)_2,2H_2O$.

B.—Silicochloroform,[3] $SiHCl_3$, is produced by cooling the gaseous products of the action of hydrochloric acid on copper silicide with liquid air; it boils at 33° (758 mm.), melts at −134°, and has a sp. gr. of 1·3438. Its decomposition by caustic soda with the production of orthosilicic acid, sodium chloride, and hydrogen has been utilised in the analysis of the compound. When heated at 800°, it is resolved into silicon tetrachloride, silicon, and hydrogen, a reaction which is reversible. Its reactions with several oxides are described, and with ammonia it gives rise to the formation of silicon nitrogen hydride, SiNH, the analogue of hydrogen cyanide, a compound difficult to free entirely from the ammonium chloride simultaneously produced. This hydride is decomposed by caustic soda, forming sodium orthosilicate, ammonia, and hydrogen. Silicofluoroform, $SiHF_3$, has also been obtained by Ruff and Albert [4] by the interaction of silicochloroform and stannic fluoride; it is a gas condensable to a liquid boiling at 80·2° (758·5 mm.), and forms a solid melting at −110°. In sealed tubes, it slowly decomposes at the ordinary temperature into hydrogen, silicon fluoride, and silicon; the decomposition is accelerated by heat. Silicofluoroform burns in air with a pale blue flame, its temperature of ignition being somewhat higher than that of the corresponding chlorine compound. It is decomposed by water and with alcohol yields ethyl orthosilicate, $Si(O{\cdot}C_2H_5)_4$, whilst with ether it forms the compound $SiH(O{\cdot}C_2H_5)_3$, ethyl orthoformate.

The production of borides, silicides, aluminides, &c., by the interaction in the electric furnace of metallic chlorides and elementary substances, for example, silicon and boron, is made the subject of a patent by Jüngst and Mewes.[5] In the reaction, a volatile chloride of silicon or boron is formed, the metal combining to form a silicide or

[1] *Ber.*, 1904, **37**, 4405.
[2] *Ibid.*, **38**, 2619.
[3] Ruff and Albert, *Ber.*, 1905, **38**, 2222.
[4] *Ber.*, 1905, **38**, 53.
[5] D.R.-P. 157615.

boride, thus calcium chloride and iron yield ferrous chloride and calcium ferride.

Hydrated metatitanic acid and some other metallic acids are violently attacked when heated with crystalline silicon, titanium trioxide being formed and hydrogen liberated; the amorphous variety of silicon does not react in this way.[1] M. Berthelot[2] has recorded experiments on the permeability of silica tubes by the gases oxygen, nitrogen, and hydrogen at high temperatures. The experiments of Mylius and Meusser[3] show that quartz vessels are not attacked by water or dilute acids at temperatures up to 100°, but are acted on by alkalis even at the ordinary temperature.

Pfeiffer[4] has found that a freshly prepared solution of stannic chloride in water gives an ethereal extract, from which light petroleum precipitates $SnCl_3OH,H_2O(C_2H_5)_2O$ in deliquescent needles which decompose at 160°. A similar compound has been obtained from stannic bromide; further, stannic bromide treated with absolute alcohol yields glistening leaflets of the compound $SnBr_3(O{\cdot}C_2H_5)(C_2H_5)_2O$.

Bellucci and Parravano[5] support their view of the constitution of stannic acid[6] by the isomorphism of potassium stannate with potassium platinate and plumbate. Perstannic acid is formed when tin dioxide is ground up with hydrogen peroxide; dried at 70°, it has the formula $HSnO_4,2H_2O$, and at 100° it forms $H_2Sn_2O_7,3H_2O$. Perstannic acid is decomposed by water; a potassium perstannate, $KSnO_4,2H_2O$, has been prepared by the action of hydrogen peroxide on potassium stannate; by continued drying it is converted into $K_2Sn_2O_7,3H_2O$. Potassium perstannate forms with water an alkaline solution which reduces potassium permanganate and sulphuric acid with a liberation of oxygen; it forms a white precipitate with lead salts, gradually decomposing with the production of lead peroxide, a fact regarded as supporting the view that the compounds are true perstannates and not substances with hydrogen peroxide of crystallisation (Tanatar).[7]

The refining of lead by the electrolytic decomposition of solutions of lead fluosilicates with an unrefined lead as anode, a method now carried out commercially, is discussed by Senn.[8] The addition of gelatine solutions is found advantageous, the copper, bismuth, and antimony in the anode remain undissolved, and the anode used contains both silica and lead fluoride. It is found impossible to separate platinum and lead by this process, owing to the formation of

[1] *Zeit. anorg. Chem.*, 1905, **43**, 370.
[2] *Compt. rend.*, 1905, **140**, 817 and 1159.
[3] *Zeit. anorg. Chem.*, 1905, **44**, 221.
[4] *Ber.*, 1905, **38**, 2466.
[5] *Atti R. Accad. Lincei*, 1905, [v], **14**, i, 457,
[6] See *Ann. Reports*, 1904.
[7] *Ber.*, 1905, **38**, 1184.
[8] *Zeit. Elektrochem.*, 1905, **11**, 229.

a crystalline compound having the formula $PtPb_2$. Cadmium may also be deposited from the solutions of its fluosilicate. The current yield with lead solutions is found to be 98 per cent. of that required by theory.

Galena and other native metallic sulphides yield the metals when heated with sodium nitrate; red lead is produced when the metal is added to the fused nitrate containing some potassium chlorate.[1] The formation of an oxyiodide by the absorption of oxygen by fused lead iodide explains, according to Schtscherbakoff[2] the anomalies observed by chemists in the electrochemical behaviour of lead iodide. This oxyiodide is formed by the action of steam on heated lead iodide and more slowly by boiling lead iodide with water. Lead iodide is stable in an atmosphere of carbon dioxide and can be sublimed in it. The production of a definite lead potassium sulphate, $K_2Pb(SO_4)_2$, is described by Belton.[3]

Group V.

A.—Nitrogen and its compounds have attracted considerable attention during the year; Baxter and Hickey[4] suggest the preparation of nitrogen by passing nitric oxide and ammonia over heated copper or platinised asbestos, whilst Hulett[5] has described a method which should be serviceable in the easy preparation of this gas. Hydrogen is burnt in a carefully regulated stream of air, and the products are passed over heated copper and copper oxide, and the nitrogen collected in the usual way. Tower[6] has found that at about 2000° nitrogen can reduce steam, forming nitric oxide and hydrogen.

The behaviour of ammonia at high temperatures and also of mixtures of nitrogen and hydrogen have been the subject of several researches. Perman[7] concludes that ammonia cannot be synthesised by heat: that it is produced by the direct union of its elements when the gases are "ionised," for example, by exploding with oxygen, by heating with many metals, or by sparking the mixed gases.[8] A method of producing ammonia industrially by the interaction of nitric oxide and hydrogen in presence of platinum black has been patented by the Westdeutsche Thomasphosphatwerke.[9] Veley[10] has shown that the liberation of ammonia from aqueous solutions of ammonium salts

[1] Matuschek, *Chem. Zeit.*, 1905, **29**, 510.
[2] *J. Russ. Phys. Chem. Soc.*, 1905, **37**, 682; also Bogorodsky, *ibid.*, 699.
[3] *Chem. News*, 1905, **91**, 191.
[4] *Amer. Chem. J.*, 1905, **33**, 300.
[5] *J. Amer. Chem. Soc.*, 1905, **27**, 1415.
[6] *Ibid.*, 1209.
[7] *Proc. Roy. Soc.*, 1905, Series *A*, **76**, 167.
[8] See also Haber and van Oordt, *Zeit. anorg. Chem.*, 1905, **46**, 111; **44**, 341; White and Melville, *J. Amer. Chem. Soc.*, 1905, **27**, 373.
[9] D.R.-P. 157287.
[10] *Trans.*, 1905, **87**, 26.

heated to boiling is due to the hydrolysis of these compounds and not to dissociation. Hydrazoic acid is formed by the oxidation of hydrazine by hydrogen peroxide and sulphuric acid.[1] The oxidation of hydroxylamine by Caro's acid yields nitroxyl, which Angelo and Angelica[2] regard as either $NH(OH)_2$ or the anhydride, NHO.

Silberrad[3] concludes, from the study of the action of zinc ethide on nitrogen iodide, that its constitution is represented by the formula $H_3N{:}NI_3$, a view supported by the investigation of its metallic compounds.[4]

The conditions favourable to the oxidation of atmospheric nitrogen in the electric arc have been investigated by Stavenhagen,[5] whilst von Lepel[6] has studied the influence of metallic salts distributed in the cathode on this oxidation.[7] Rossi[8] has noted the production of nitric oxides by the action on compressed air of incandescent bodies, such as the filament in the Nernst lamp. It is suggested that the yield is sufficient to be of industrial importance in the manufacture of nitric acid.

An interesting method for the production of a mixture of nitric oxide and nitrogen peroxide is that described by Matuschek,[9] dependent on the interaction in aqueous solutions of ferric chloride and sodium nitrite.

Rây[10] has continued his researches on the nitrites, discussing the conditions influencing the formation of ten different products of the action of nitric acid on mercury. This author[11] has also prepared the nitrites of alkali- and alkaline-earth metals which are formed by the interaction of the chlorides on silver nitrite. The solutions of these nitrites may be evaporated in contact with the air without undergoing oxidation. These nitrites have a yellow colour, the depth of which increases with the atomic weight of the metal. Magnesium nitrite is the least stable of those of the alkaline earths forming, as magnesium does in many other cases, a link between the nitrites of zinc and cadmium and those of calcium, strontium, and barium.

Rây and Gañguli[12] have recently described two varieties of silver nitrite, the one having the formula $AgNO_2$, the other the formula AgONO; but Divers[13] has shown that the evidence advanced by these authors in support of the existence of these two varieties is capable of another interpretation.

[1] Browne, *J. Amer. Chem. Soc.*, 1905, **27**, 551.
[2] *Gazzetta*, 1905, **35**, [i], 152.
[3] *Trans.*, 1905, **87**, 55.
[4] *Ibid.*, 66.
[5] *Ber.*, 1905, **38**, 2171.
[6] *Ibid.*, 2524.
[7] See also Scheuer, *Zeit. Elektrochem.*, 1905, **11**, 563.
[8] *Gazzetta*, 1905, **35**, [i], 89.
[9] *Chem. Zeit.*, 1905, **29**, 31.
[10] *Trans.*, 1905, **87**, 171.
[11] *Ibid.*, 175.
[12] *Proc.*, 1905, **21**, 279.
[13] *Ibid.*, 281.

Nitroxyl fluoride (NO_2F) is formed by the action of nitric oxide on fluorine at the temperature of liquid oxygen. It is a colourless gas, which attacks the mucous membrane; it has been solidified and melts at $-139°$, forming a liquid boiling at $-63{\cdot}5°$. The discoverers of this compound, Moissan and Lebeau,[1] describe its reactions with a number of substances, the decomposition by water yielding hydrofluoric and nitric acids, which reaction has been utilised in its analysis. Nitrosyl fluoride, NOF, formed, according to Ruff and Stäuber,[2] by the action of silver fluoride on nitrosyl chloride, resembles fluorine and nitroxyl fluoride, but differs from these in its density and action in water. Ruff and Geisel,[3] continuing their researches on nitrogen sulphide [4] find the solution of sulphur in liquid ammonia affords a method of preparing the sulphide. The action of sulphur and liquid ammonia resulting in the formation of hydrogen and nitrogen sulphides is a reversible one, the removal of the former as silver sulphide by means of silver iodide dissolved in ammonia favouring the formation of the nitrogen sulphide, which can be obtained by evaporating off the ammonia from the filtrate left after the removal of the silver sulphide. The blue colour of the solution of sulphur in liquid ammonia is attributed to colloidal sulphur.

B.—It would appear that the term red phosphorus embraces a number of modifications; a scarlet variety is described by Schenck;[5] it is deposited from the solutions of phosphorus in phosphorus iodide, sulphide (P_4S_3), or tribromide. The scarlet modification is an amorphous solid which phosphoresces in ozone, but not in air; it is dissolved by alcoholic potash, from which solution acids precipitate the hydride $P_{12}H_6$, and when heated it is converted into the red modification. The phosphorescence of phosphorus is not, according to Jungfleisch,[6] due to combustion of phosphorus, but to the formation of an oxide which is more volatile than phosphorus, and which, by its spontaneous combustion, gives rise to the phenomenon in question. The subiodide of phosphorus, P_4I, is produced by the action of dry iodine on phosphorus dissolved in carbon disulphide; with alkalis, it reacts to form the suboxide, $P_4(OH)$.[7] Stock and Thiel [8] have prepared the pentasulphide by heating the solution of phosphorus and sulphur in carbon disulphide at 120—130° with a trace of iodine. The pentasulphide in appearance resembles the flowers of sulphur, and exists in two varieties, differing in solubility in carbon disulphide, the less readily soluble form having a molecular formula, P_4S_{10}, whilst the other variety appears to have a lower molecular weight.

[1] *Compt. rend.*, 1905, **140**, 1573 and 1621.
[2] *Zeit. anorg. Chem.*, 1905, **47**, 190.
[3] *Ber.*, 1905, **38**, 2659.
[4] See *Ann. Reports*, 1904.
[5] *Zeit. Elektrochem.*, 1905, **11**, 117.
[6] *Compt. rend.*, 1905, **140**, 444.
[7] Boulough, *Compt. rend.*, 1905, **141**, 256.
[8] *Ber.*, 1905, **38**, 2719.

Stock and Siebert[1] describe another mode of formation of the yellow modification of arsenic, and Lockemann[2] has drawn attention to the catalytic decomposition of arsine by cotton wool, glass wool, or alcohol, an observation of importance in connection with the detection of arsenic by the Marsh test.

The halogen double salts of tervalent antimony are colourless, those of quinquevalent antimony have a slightly green tint, whilst the double salts containing quadrivalent antimony are strongly coloured. The latter are formed by taking a solution of antimony trichloride, dividing it into two equal parts, one half after oxidation with chlorine being added to the other portion. Such a mixture contains the chloride of quadrivalent antimony

$$SbCl_3 + SbCl_5 \rightleftarrows 2SbCl_4,$$

the proportion depending on the temperature and concentration of hydrogen chloride. By adding rubidium chloride and hydrochloric acid to such solutions containing $SbCl_4$, Rb_2SbCl_6 is formed as a black, crystalline powder; the corresponding ammonium and pyridine salts have been prepared. These and other double halides are described by Weinland and Schmidt,[3] who, by treatment of the solution of antimony trioxide in hydrochloric acid with chlorine, and subsequently with hydrogen chloride, have obtained metachlorantimonic acid, $HSbCl_6,4\frac{1}{2}H_2O$, in the form of greenish-yellow, hygroscopic prisms. The authors describe a series of ammonia metachlorantimonates, as also pyridine and quinoline salts of this acid,[4] thus:

$AgSbCl_6,2NH_3$, $Cu(SbCl_6)_2,5NH_3$, $HSbCl_6,C_5H_5N$, and $HSbCl_6,C_9H_7N$.

Group VI.

A.—The production of oxygen from bleaching powder by the simultaneous action of a ferrous or manganous salt with a salt of copper, nickel, or cobalt is patented by Jaubert.[5] Julius Meyer[6] considers the facts of auto-oxidation are best explained on the assumption that an unsaturated molecule is added to a molecule of oxygen, one atom of which functions as a quadrivalent atom. The grouping O:O: is probably more common and more stable than that of two quadrivalent oxygen atoms, just as in the case of nitrogen compounds the grouping N‴:N′ is more common and stable than two quinquevalent nitrogen atoms. Hydrogen peroxide is, therefore, regarded as $O{:}OH_2$, existing in the unimolecular state only, whereas water in the bimolecular form is $H_2O{:}OH_2$. The formulæ are proposed for the peroxides:

[1] *Ber.*, 1905, **38**, 966.
[2] *Zeit. angew. Chem.*, 1905, **18**, 491.
[3] *Ber.*, 1905, **38**, 1080.
[4] *Zeit. anorg. Chem.*, 1905, **44**, 37.
[5] D.R.-P. 157171.
[6] *J. pr. Chem.*, 1905, [ii], **72**, 278.

ozone, O:O:O, barium peroxide, O:OBa, potassium peroxide, $O{:}OK_2$, and sodium hydrogen peroxide, O:OHNa. McIntosh[1] has continued his researches on the basic properties of oxygen and materially extended the list of compounds formed by alcohol, ether, and acetone with acids and acidic elements, the formation of which is most readily explained by assuming that the oxygen contained in these organic substances is quadrivalent at low temperatures. The production of ozone by the ultra-violet light produced by the mercury arc lamp has been investigated by Fischer and Braehmer,[2] who find that no ozone is formed at temperatures above 270°, and conclude that the production of ozone by the silent electrical discharge is probably due to the action of light, as Warburg has shown that in the silent electrical discharge both ultra-violet rays and cathode rays are produced.

Chromium deposited electrolytically from solutions of chromic acid occludes about 250 times its volume of hydrogen.[3] Colson's researches on the sulphates of chromium show that a normal green sulphate, $Cr_2(SO_4)_3,10H_2O$, is formed by reducing a solution of chromic acid with sulphur dioxide at 0°. This sulphate is isomeric with violet chromium sulphate, and by boiling its aqueous solutions a pentasulphate is formed, for which the formula $SO_4\left(Cr<\begin{matrix}SO_4\\O\end{matrix}>CrSO_4\right)_2$ is proposed,[4] the green sulphate being $SO_4<\begin{matrix}Cr{:}SO_4\\|\\Cr{:}SO_4\end{matrix}$. Potassium and ammonium chromoxalates form isomorphous mixtures; these complex salts can, as has been proposed by Cameron,[5] be derived from $Cr(OH)_3$ by the step by step replacement of the hydroxyl groups by univalent radicles $(C_2O_4M)'$, thus $Cr(C_2O_4K)_3$, $OH{\cdot}Cr(C_2O_4K)_2$, and so on. The researches of Riesenfeld, Wohlers, and Kutch[6] on the higher oxidation products of chromium show that the oxidation of ammonium chromate by hydrogen peroxide yields, according to the proportion of peroxide used, either red salts or blue salts, and not the substances described by Hofmann and Hiendlmaier.[7] The red salts are derivatives of an acid H_3CrO_8, whilst the blue salts correspond to the acid H_3CrO_7. In neutral or alkaline solutions, the red salts are decomposed to chromates, whilst in acid solutions blue perchromic acid is first formed, rapidly passing into a chromic salt. From the blue ethereal solutions of perchromic acid, Byers and Reid[8] have prepared a number of salts of this acid. The

[1] *Trans.*, 1905, **87**, 784, and *J. Amer. Chem. Soc.*, 1905, **27**, 1013.
[2] *Ber.*, 1905, **38**, 2633.
[3] *J. Physical Chem.*, 1905, **9**, 353.
[4] *Compt. rend.*, 1905, **140**, 42, 372, 1451; **141**, 114, 331.
[5] *Proc. Roy. Soc. Edin.*, 1905, **25**, 727.
[6] *Ber.*, 1905, **38**, 1885.
[7] See *Ann. Reports*, 1904.
[8] *Amer. Chem. J.*, 1904, **32**, 503.

potassium salt, $KCrO_4$ or $K_2Cr_2O_8$, is formed as a purplish-black solid by the action of potassium on the ethereal solution at $-20°$.

Molybdenum[1] can be obtained by the Goldschmidt method, using fluorspar as flux. The insoluble trichloride, $MoCl_3$, resembles red phosphorus in appearance and reacts with gaseous ammonia at 340° to form a black solid, $Mo_2(NH_3)_3Cl_3$, which at 760° decomposes and gives the nitride Mo_3N_2 as a metallic powder. The insoluble tribromide, $MoBr_3$, prepared like the chloride by Blomstrand's method, forms black needles, and is converted into the metal by ammonia. The soluble chloride, prepared by electrolysing the solutions of molybdenum trioxide in hydrochloric acid, gives on treatment with potassium fluoride crystalline potassium molybdenum fluoride, $KMoF_4,H_2O$.

By the interaction of tungsten hexachloride and hydrogen fluoride at low temperatures, Ruff and Eisner[2] have obtained the gaseous hexafluoride, WF_6, which is the heaviest gas known, being ten times as heavy as an equal volume of air; it is a very active compound, attacking glass and metals. The use of tungstic trioxide as a glaze on porcelain is limited by the fact that it becomes opaque at high temperatures, but by fusing it at 800° with lead silicate or a mixture of zinc borate and silicate Granger has succeeded in obtaining a permanent yellow glaze.[3]

B.—In molten sulphur there appear to be two varieties of the element which are only partially miscible, namely, S_λ, a yellow, mobile form which predominates at temperatures between the melting point and 160°, and S_μ, a brown, viscous form which constitutes the chief portion above 160°.[4] Sulphur is soluble in benzyl chloride, and separates from its solution in this medium in rhombic crystals.[5] The primary action of alkali hydroxides on sulphur is suggested by Pomeranz[6] to be similar at the outset to their action on chlorine in the cold, and to result in the production of a sulphide and a hyposulphite. The formation of polysulphides and thiosulphates is due to subsequent reactions. The action of sulphur and sodium hydroxide under the above-mentioned conditions may be represented as follows:

$$S_2 + 3NaOH = NaHSO_2 + Na_2S + H_2O.$$

Solutions containing sulphur and caustic soda bleach *p*-nitraniline-red, as sodium hyposulphite does. The composition attributed to the hyposulphite is, it will be noted, at variance with Bernthsen's formula,

[1] Rosenheim and Braun, *Zeit. anorg. Chem.*, 1905, **46**, 311.
[2] *Ber.*, 1905, **38**, 742. [3] *Compt. rend.*, 1905, **140**, 935.
[4] Smith, *Proc. Roy. Soc. Edin.*, 1905, **28**, 588, 590.
[5] Boguski, *J. Russ. Phys. Chem. Soc.*, 1905, **37**, 92.
[6] *Zeit. Farb. Text. Ind.*, 1905, **4**, 392.

who adheres to the view that the sodium salt is $Na_2S_2O_4,2H_2O$, and not a double salt of the composition $NaHSO_3,NaHSO_2,H_2O$. Bernthsen [1] has suggested that the name "hyposulphite" should be restricted to the salts $R'_2S_2O_4$, and that salts $RHSO_2$ and R_2SO_2 should be styled "sulphoxylites." Several authors have busied themselves with the preparation and properties of the hyposulphites, and Billy [2] states that the sodium salt is not formed by the action of sulphur dioxide on sodium amalgam in presence of ether or light petroleum unless a trace of alcohol be present. Observations on the oxidation of sodium hyposulphite have been made by A. Lumière, L. Lumière, and Seyewetz,[3] and by Binz.[4]

The contact process for the manufacture of sulphuric acid has been the subject of several researches; Küster [5] has found platinum to be the most efficient catalytic agent and the only one of technical importance; Bodenstein and Pohl,[6] also Lucas,[7] have investigated the equilibrium between sulphur dioxide, oxygen, and sulphur trioxide.

From the cryoscopic study of the solutions of copper sulphate, Colson [8] concludes that the molecular complexity of this compound is $(CuSO_4)_2$, and that the composition of the sulphates of bivalent metals in aqueous solutions is represented by the formula $(HSO_4M'')_2O$; the sulphates are supposed to be formed by the condensation of two molecules of sulphuric acid with hydroxides of the formula $(OHM'')_2O$. Many of the reactions of such sulphates, for example, their acidic properties, are readily explained by these assumptions.

Hantzsch and Stuer [9] conclude that the gelatinous product formed when sulphuryl chloride dissolved in light petroleum is attacked by ammonia is probably ammonium *aci*-sulphomelide, $S_3O_3N_3(ONH_4)_2$, sulphomelide being the analogue of cyamelide, formed by the action of ammonia on carbonyl chloride in light petroleum. Sulphomelide forms salts, whereas cyamelide does not; whilst sulphomelide has the constitution $NH{:}SO\langle^{O\cdot SO\cdot NH}_{O\cdot SO\cdot NH}\rangle O$, and is a pseudo-acid, the *aci*-sulphomelide would be $OH\cdot NS\langle^{O\cdot NS(OH)}_{O\cdot NS(OH)}\rangle O$, a true acid. Further, it is shown that the trisulphimide described by Hantzsch and Holl is in reality iminosulphonamide, $NH_2\cdot SO_2\cdot NH\cdot SO_2\cdot NH_2$, formed by the action of water on trisulphimide, thus:

$$NH\langle^{SO_2\cdot NH}_{SO_2\cdot NH}\rangle SO_2 + 2H_2O = NH_2\cdot SO_2\cdot NH\cdot SO_2\cdot NH_2 + H_2SO_4.$$

[1] *Ber.*, 1905, **38**, 1048; see also Prud'homme, *Bull. Soc. chim.*, 1905, [iii], **33**, 129; and Bazlen, *Ber.*, 1905, **38**, 1057.
[2] *Compt. rend.*, 1905, **140**, 936.
[3] *Bull. Soc. chim.*, 1905, [iii], **33**, 931.
[4] *Zeit. Farb. Text. Ind.*, 1905, **4**, 161.
[5] *Zeit. anorg. Chem.*, 1904, **42**, 453.
[6] *Zeit. Elektrochem.*, 1905, **11**, 373.
[7] *Ibid.*, 1905, **11**, 457.
[8] *Compt. rend.*, 1904, **139**, 857.
[9] *Ber.*, 1905, **38**, 1022.

Iminosulphonamide is a monobasic acid, moderately stable towards alkalis, forming salts of the type $RN(SO_2 \cdot NH_2)_2$, which by an excess of alkali are resolved into ammonia and aminosulphonates.

Double sulphates of uranyl and the alkali metals, for example, $K_2SO_4,UO_2SO_4,2H_2O$, are described by de Coninck and Chauvenet;[1] these compounds are formed by the action under pressure of acid sulphates of the alkali metals on uranic hydroxide.

Magnesium powder, when heated with an anhydrous sulphate, reacts with very considerable energy; in all cases excepting that of the alkali sulphates, sulphur dioxide is produced, frequently sulphur, magnesia, the oxide, sulphide, and thiosulphate of the metal. Sulphur trioxide passed over heated magnesium gives sulphur dioxide, oxide, and sulphide of magnesium (Brückner).[2] Colloidal modifications of selenium and tellurium are formed by the reduction of selenious or telluric acids by hydroxylamine or hydrazine in presence of sodium protalbate or lysalbate.[3] The precipitates formed by the action of hydrogen sulphide on selenious acid are mixtures of selenium and sulphur.[4] Uranyl selenide, UO_2Se, formed by heating together selenium, potassium cyanide, and uranium oxide, is described by Milbauer,[5] who, by replacing uranium oxide by chromium sesquioxide, has obtained potassium chromic selenide, $K_2Cr_2Se_4$.

Hutchins,[6] from a careful revision of the preparation and properties of the tellurates, concludes that there are no well authenticated cases of isomorphism amongst the tellurates and sulphates.

Group VII.

A.—Of manganese there is little to record beyond the borides already mentioned. Four manganous sulphides exist according to Olsen and Rapalje;[7] the red and green are anhydrous, a grey variety contains a large proportion of water, whilst the pink sulphide is a mixture of the grey and red. A double chromate of potassium and manganese, $K_2CrO_4,MnCrO_4,2H_2O$, crystallising in red prisms, has been prepared by Gröger;[8] the production of manganese chromates by the action of soluble chromates on manganese chloride is rendered difficult by the ready decomposition of manganous chromate into chromium manganite, $(Cr_2(MnO_3)_3)$, and chromic anhydride. The absorption spectrum of carefully prepared manganous chloride has been shown to consist of

[1] *Bull. Acad. roy. Belg.*, 1905, **7**, 50, 94, 151, 182.
[2] *Monatsh.*, 1905, **26**, 675.
[3] Paal and Koch, *Ber.*, 1905, **38**, 526 and 534.
[4] Gutbier and Lohmann, *Zeit. anorg. Chem.*, 1905, **43**, 384.
[5] *Ibid.*, 1904, **42**, 450.
[6] *J. Amer. Chem.*, 1905, **27**, 1157.
[7] *J. Amer. Chem. Soc.*, 1904, **26**, 1615.
[8] *Zeit. anorg. Chem.*, 1905, **44**, 453.

(1) a broad band λ513—λ557·5, (2) a less intense band, λ420—λ442·5, and (3) a group of six bands from λ410—λ695.[1]

B.—An examination of the properties of hydrofluoric acid has been made by Deussen,[2] who from the manner in which it affects the inversion of cane sugar places this acid with the weak acids, such as chloracetic acid. Hydrofluoric acid may be titrated by caustic soda or potash with phenolphthalein as indicator; it interferes with the titration of ferrous salts by potassium permanganate. In the separation of alumina from ferric oxide when the former predominates, Deussen recommends fusion with potassium hydrogen fluoride. The removal of rust from iron is readily affected by hydrofluoric acid. Ruff and Thiel[3] have found in the action of hydrofluoric acid on nitrogen sulphide and copper oxide a method of preparing thionyl fluoride. The fluoride in presence of carbon or of sunlight reacts with chlorine and silica, forming silicon tetrafluoride and sulphuryl fluoride, and with nitrogen trioxide and traces of moisture it reacts with silica, forming nitrosulphonic acid and silicon tetrafluoride. A series of fluorides of the heavy metals has been prepared by Böhm.[4]

Russ's[5] researches on the "activation" of chlorine by the simultaneous action of light and of the silent electrical discharge, the retention of this activity, and other facts, indicate that the question is still an open one whether the "activation" is due to the formation of a modified chlorine or to the production of intermediate compounds. Foster,[6] however, shows that there are no such changes, for example, in density, as would justify the acceptance of the conclusion that a new modification of chlorine is formed in this way.

Levi and Bettoni[7] conclude that the Deacon process for the manufacture of chlorine depends on the joint action of high temperature and the porous materials used in the towers, the copper salt accelerating the interaction between the hydrochloric acid and the air by absorbing the water formed in the reaction. A new explanation of the formation and constitution of bleaching powder is that brought forward by Tarugi.[8] As oxygen influences the formation of a bleaching powder containing the maximum proportion of active chlorine, and hydrated lime left in contact with the air contains peroxide, the formation of bleaching powder may be explained as depending on: firstly, the formation of oxygen by the action of chlorine on water; secondly, the oxygen converting the calcium hydroxide into the compound CaO_2,H_2O_2, which by hydrochloric

[1] Lambert, *Compt. rend.*, 1905, **141**, 357.
[2] *Zeit. anorg. Chem.*, 1905, **44**, 300 and 408.
[3] *Ber.*, 1905, **38**, 549.
[4] *Zeit. anorg. Chem.*, 1905, **43**, 326.
[5] *Ber.*, 1905, **38**, 1310.
[6] *Ibid.*, 1781.
[7] *Gazzetta*, 1905, **38**, [i], 320.
[8] *Ibid.*, 1904, **34**, [ii], 254.

acid formed in the first reaction is converted into CaO_2Cl_2, that is, the chloride of the peroxide, the hypochlorites being regarded as the chlorides of the peroxides. Bleaching powder containing 44·09 per cent. of active chlorine would have the formula CaO_2Cl_2,H_2O. This compound is decomposed quantitatively by mercury into calcium peroxide and mercuric chloride.

By the action of hydroxylamine on aqueous solutions of metallic chlorides, double salts are formed which can be precipitated from these solutions by alcohol; the following will serve as examples of the series of compounds: $MgCl_2,2NH_2OH,2H_2O$; $CaCl_2,2NH_2OH,H_2O$; $ZnCl_2,2NH_2OH$.[1]

Group VIII.

Experimenting on the reduction of ferric and of ferrous oxide by a mixture of equal volumes of carbon monoxide and carbon dioxide when "dry" and "moist," Boudouard [2] has found the dry gas more efficient at temperatures up to 800°, but above that temperature and up to 1050° there is little difference between moist and dry gas. The researches of Schenck and Heller [3] on the reactions involved in the reduction of iron are of considerable importance. When carbon monoxide is heated with metallic iron, the pressure observed after equilibrium is established is extremely small, and apparently all the gas is removed. This arises from the oxidation of the iron and the deposition of the carbon in the solid form. Pure carbon monoxide cannot oxidise iron; it is assumed that the iron acts firstly catalytically, decomposing the carbon monoxide into carbon and carbon dioxide, secondly, reducing the carbon dioxide to carbon monoxide with the simultaneous formation of ferrous oxide; thus, the end equilibrium is twofold, as represented by the equations:

$$(1)\ 2CO \rightleftarrows C + CO_2.$$
$$(2)\ FeO + CO \rightleftarrows Fe + CO_2.$$

The partial pressures of the two oxides of carbon and their sum are dependent on the temperature only, or for each temperature there is a definite partial pressure for each oxide and also a definite total pressure. It follows that in the blast furnace ferrous oxide will only be reduced by carbon monoxide in the presence of carbon if the total pressure of the carbon monoxide and dioxide is less than the pressure of the total equilibrium, whereas, when the pressure of the gas mixture at the given temperature is greater, the reoxidation of iron and

[1] Antonoff, *J. Russ. Phys. Chem. Soc.*, 1905, **37**, 476.
[2] *Compt. rend.*, 1905, **140**, 142; also **141**, 252.
[3] *Ber.*, 1905, **38**, 2132.

deposition of carbon take place. The pressure for the total equilibrium has been determined for temperatures between 400° and 800°; firstly, by heating carbon monoxide with finely-divided iron and measuring the pressure when equilibrium is established; secondly, by heating ferrous oxide and carbon in a vacuum and determining the pressure at fixed temperatures. Applying this last method with different varieties of carbon, the authors[1] have shown that at the same temperature the highest pressures are given by amorphous carbon and the lowest with graphite, powdered diamond being intermediate between the two. The powdered carbon obtained by decomposing carbon monoxide comports itself like graphite. Consequently for a given temperature in a blast furnace worked with wood charcoal the gaseous mixture will be richer in carbon monoxide than in a furnace worked with coke. The fact that iron saturated with carbon expands on solidifying, whereas pure iron behaves normally, is shown by Moissan[2] to be an important factor in the formation of the diamond by his method. Iron is deposited electrolytically most satisfactorily by employing a solution of ferrous and magnesium sulphates, to which a small proportion of sodium bicarbonate is added; a skin of ferric hydroxide thus formed on the surface serves to protect the solution from oxidation. Wrought iron is used as anode, and copper, thinly silvered, is used as cathode.[3] Of the researches on the question of the rusting of iron, special mention should be made of the complete and thorough examination made by Dunstan, Jowett, and Goulding,[4] from which it appears that iron, oxygen, and liquid water are alone essential to the phenomenon, the carbon dioxide of the air playing but a small part. The explanation advanced assumes the production of hydrogen peroxide, although its formation has not been demonstrated. The analyses of rust produced in different experiments agree satisfactorily with the formula $Fe_2O_2(OH)_2$. Divers[5] contends that the production of hydrogen peroxide is unnecessary to the explanation of the observations of the authors.

Despite the sensitiveness to air, moisture, and light exhibited by iron carbonyl, Dewar and Jones,[6] have succeeded in establishing its composition as iron pentacarbonyl, $Fe(CO)_5$; the physical constants have been determined and in its chemical reactions it has been found to comport itself like nickel carbonyl.[7] By the action of light it is converted into the compound $Fe_2(CO)_7$, the production of which is explained

[1] *Ber.*, 1905, **38**, 2139. [2] *Compt. rend.*, 1905, **140**, 185.

[3] Maximowitsch, *Zeit. Elektrochem.*, 1905, **11**, 52.

[4] *Trans.* 1905, **87**, 1548; see also Cribb and Arnaud, *Analyst*, 1905, **30**, 225; Lindet, *Compt. rend.*, 1904, **139**, 859.

[5] *Proc.*, 1905, **21**, 251.

[6] *Proc. Roy. Soc.*, 1905, Series *A*, **76**, 558. [7] See *Ann. Reports*, 1904.

by assuming that the pentacarbonyl is partly resolved into the tetracarbonyl, $Fe(CO)_4$, and carbon monoxide, the tetracarbonyl combining with iron pentacarbonyl to form $Fe_2(CO)_9$. Consistently with these conclusions, nickel carbonyl and iron carbonyl should form $FeNi(CO)_9$; the coloration observed when nickel carbonyl is dissolved in iron carbonyl is regarded as a confirmation of these views.

Hauser [1] has obtained a new class of complex iron compounds from the solutions formed by the treatment of both ferrous and ferric salts with an excess of ammonium carbonate. Iron phosphide, Fe_2P, is formed by heating calcium phosphate with metallic iron and silica in the electric furnace.[2] Lipschitz and von Hasslinger [3] find that pure ferrous sulphide is but slightly attacked by dilute acids, whereas when it contains metallic iron the iron sulphide is readily dissolved. The iron is first dissolved by the acid, and the hydrogen so formed attacks the iron sulphide, forming sulphuretted hydrogen and metallic iron. Consequently the small amount of iron in the ferrous sulphide acts as an accelerator.

The physical constants of pure nickel and cobalt have been determined by Copaux; [4] the pure metals were prepared from carefully purified oxalates. Cobalt is silvery-white in colour, whereas nickel is comparatively dull, and both have a specific gravity of 8·8; cobalt melts at 1530° and nickel at 1470°; Guertler and Tammann [5] give the melting points of these metals as 1528° and 1484° respectively. Cobaltic fluoride, CoF_3, is formed as a green powder by electrolysing a solution of cobalt fluoride in hydrofluoric acid, using a platinum dish as anode; nickel fluoride does not yield a nickelic compound (Barbieri and Calzolari).[6] When a current of electricity is passed through a solution of caustic soda or potash, using cobalt as the anode, a blue solution is formed, which Tubandt [7] regards as containing cobaltous oxide in a colloidal form. Tubandt [8] has also noted the production of a deep red solution on electrolysing nickel carbonate in presence of potassium hydrogen carbonate; the colour is due to the formation of an unstable nickelic salt. Our knowledge of the cobaltammine salts has been extended by the researches of Werner and his pupils.[9] The cobaltammines richest in ammonia are of the type $[Co(NH_3)_6]X_3$; other saturated compounds containing two atoms of cobalt of the type $X_2[Co(NH_3)_5NH,Co(NH_3)_5]X_2$ have been prepared, as also derivatives from the same in which two NH_3 groups are replaced by pyridine, thus: $Cl_2[CoPy(NH_3)_4NHCo(NH_3)_4Py]Cl_2$. Dibromotetra-ammine

[1] *Ber.*, 1905, **38**, 2707.
[2] Gin, D.R.-P. 156087.
[3] *Monatsh.*, 1905, **26**, 217.
[4] *Compt. rend.*, 1905, **140**, 651.
[5] *Zeit. anorg. Chem.*, 1904, **42**, 353.
[6] *Atti R. Accad. Lincei*, 1905, [v], **14**, 464.
[7] *Zeit. anorg. Chem.*, 1905, **45**, 368.
[8] *Ibid.*, 73.
[9] *Ber.*, 1905, **38**, 923, 992, 2009.

cobalt bromide, $[Br_2Co(NH_3)_4]Br$, is obtained as a green, amorphous solid by the action of hydrobromic acid on the carbonate; the bromide treated with hydrochloric acid gives the chloride, which by water is converted into the aquo-salt, $[Br(H_2O)Co(NH_3)_4]ClBr$, forming reddish-violet solutions. This compound belongs to a series intermediate between the diaquotetra-ammine salts, $[(H_2O)_2Co(NH_3)_4]Br_3$, and dibromotetra-ammine series, for example, $[Br_2Co(NH_3)_4]Br_2$. By the action of hydroxylamine hydrochloride on dichlorodiethylenediamine cobalt chloride or on chlorohydroxylaminediethylenediamine cobalt chloride in aqueous caustic potash solutions, hexahydroxylamine cobalt chloride, $[Co(NH_2OH)_6]Cl_3$, is formed, which crystallises in large, golden leaflets.[1]

By employing hydrazine hydrate to reduce dilute solutions of salts of the platinum metals in presence of gum arabic, Gutbier and Hofmeier[2] have obtained hydrosols of these metals. The hydrosols may be obtained in the solid form by evaporating the solutions in a vacuum over strong sulphuric acid. Paal and Amberger have also investigated the precipitation of palladium by hydrazine hydrate and the production of the metal as a hydrosol, which is effected by treating solutions of palladium chloride with hydrogen in presence of sodium protalbate.[3] These authors find that the dry hydrosol obtained by evaporating the solution in a vacuum renders hydrogen sufficiently active to be able to reduce nitrobenzene in alcoholic solutions to aniline, whereas palladium black and the hydrogel of this metal have no such power. Gutbier and Krell[4] have described a series of ammonium, cæsium, and rubidium palladichlorides and palladochlorides of the types R_2PdCl_6 and $R_2'PdCl_4$ respectively. Wöhler and König[5] show that there are only two oxides of palladium, namely, palladic oxide, PdO_2, which is formed either by the action of ozone on palladium salts or by the anodic electrolytic oxidation, and palladous oxide, PdO, which is obtained by boiling faintly acid nitrate solutions with water. The palladic oxide, which is readily decomposed into the lower oxide and oxygen, acts as an oxidising agent and decomposes hydrogen peroxide.

Ruthenium is obtained by reducing the oxide, Ru_2O_4, with alcohol and finally heating the product in a stream of hydrogen. Gutbier and Trenkner[6] have been unsuccessful in their attempts to obtain a dichloride and a tetrachloride, but readily obtained the chloride Ru_2Cl_6 by Claus's method. These authors have also prepared double salts of this chloride with those of rubidium and cæsium. Ruthenium bromide

[1] Werner and Berl, *Ber.*, 1905, **38**, 893.
[2] *J. pr. Chem.*, 1905, [ii], **71**, 358 and 452.
[3] *Ber.*, 1905, **38**, 1388, 1394, 1398, 1406.
[4] *Ibid.*, 2385.
[5] *Zeit. anorg. Chem.*, 1905, **46**, 323.
[6] *Ibid.*, **45**, 166.

and iodide are also described, as are the compounds which they form with ammonia, analogous in composition to Joly's $Ru_2Cl_6,7NH_3$. Ruthenium dioxide, RuO_2, is obtained in the form of blue plates by heating the metal in oxygen, and is also produced by the ignition of the sulphate. The sesquioxide, Ru_2O_5, can be obtained by heating the hydroxide formed by the action of caustic potash on the trichloride. Attempts to obtain the oxides described by Joly and Debray were unsuccessful (Gutbier and Ramsohoff).[1]

Double nitrites of osmium with nitrites of sodium, ammonium, silver, and of the nitrites of the metals of Group II are described by Wintrebert.[2] They are for the most part yellow, crystalline solids. By decomposing the barium salt, $BaOs(NO_2)_5,4H_2O$, with dilute sulphuric acid, a solution of osminitrous acid, $H_2Os(NO_2)_5$, is formed, which, on evaporation, leaves osmium nitrite as a deep brown powder. Potassium iridochloronitrite, $K_{12}Ir_3Cl_{16}(NO_2)_8,4H_2O$, is formed by evaporating potassium iridium nitrite to dryness with dilute nitric acid and dissolving the residue in a solution of potassium chloride, from which the iridochloronitrite separates out (Quennessen).[3] Hussak[4] has described the mode of occurrence of platinum and palladium in Brazil. On the volatilisation of platinum, Hulett and Berger[5] note that the metal begins to volatilise in air at 800°, whereas no volatilisation is observed if oxygen be absent. This observation has led to the suggestion that an oxide is formed which decomposes at 800°. Lucas[6] finds that platinum begins to absorb oxygen at 615°, and the rate increases up to 1000°, from which point it begins to fall. This is only true of platinum containing iridium, as pure platinum does not absorb the gas.

The alteration in appearance which platinic hydroxide, $PtO_2,4H_2O$, undergoes when dried is explained by Blondel[7] as being due to its conversion into $H_2Pt(OH)_6$.[8] In platinic hydroxide, two of the hydroxyl groups are acidic, whilst another two are basic, consequently it forms platinates of the type $Pt(OH)_4,2M'OH$, where M′ is an alkali metal, and with acids salts like the chloride, $Pt(OH)_4,2HCl$, which compound is formed by dissolving the hydroxide in dilute hydrochloric acid. It gives no precipitate with a potassium salt, but in course of time passes into chloroplatinic acid. Potassium platinoso-oxalate, when oxidised by potassium permanganate, forms the platinic oxalate,

$$K_2PtO(C_2O_4)_2,2H_2O,$$

from the silver salt of which has been prepared the acid

$$H_2PtO(C_2O_4)_2,5H_2O,$$

crystallising in amber tablets and detonating violently when heated.

[1] *Zeit. anorg. Chem.*, 1905, **45**, 243.
[2] *Compt. rend.*, 1905, **140**, 585.
[3] *Ibid.*, **141**, 258.
[4] *Chem. Centr.*, 1905, [ii], 107.
[5] *J. Amer. Chem. Soc.*, 1904, **26**, 1512.
[6] *Zeit. Elektrochem.*, 1905, **11**, 182.
[7] *Ann. Chim. Phys.*, 1905, [viii], **6**, 81.
[8] See *Ann. Reports*, 1904.

Guillet's[1] researches on the constitution and properties of steels show that up to 2 per cent. aluminium has but little influence on the properties of steel, further, that up to 15 per cent. this metal dissolves in the iron, and the solution does not dissolve carbon. The structure of ordinary steels is not affected by tin up to 0·5 per cent., whereas when the tin is between 5 and 10 per cent. it dissolves in the iron and separates in the form of a definite compound; in such steels the carbon exists as carbide, and there is no graphite present. Titanium up to 9 per cent. does not change the structure of steel; the mechanical properties are but slightly altered; in steels containing 0·7 per cent. of carbon, the breaking strain is much improved by the presence of titanium. The mechanical properties are but little affected by cobalt; the perlitic structure is shown in steels containing up to 60 per cent. cobalt.

Ternary steels are grouped by Guillet as follows: (1) perlitic; (2) martensitic, including troostitic; (3) γ-iron; (4) carbide, and (5) graphitic steels. Braune[2] has observed that iron heated at 800° in an atmosphere of ammonia forms iron nitride, which, forming a solid solution with iron, lowers its melting point and reduces its ability to dissolve carbon. By annealing, the nitride can be made to diffuse equally through the iron. The tensile strength increases with the proportion of nitrogen, whilst the ductility falls rapidly. Steel containing 1·15 per cent. of carbon becomes brittle with 0·04—0·045 per cent. of nitrogen. Le Chatelier[3] considers that Braune's observations explain the difference in brittleness frequently observed in steels of identical composition. Le Chatelier points out that iron does not combine directly with atmospheric nitrogen, but in presence of basic slag and of reducing agents this combination takes place. Consequently the absorption of nitrogen takes place chiefly in the blast furnace and in the basic-converter, and is probably due to the formation of cyanides. Inferior qualities of iron are, as is well known, produced in furnaces in which much potassium cyanide is formed.

P. Phillips Bedson.

[1] *Compt. rend.*, 1905, **141**, 35; **140**, 1689; **141**, 107.
[2] *Rev. Metallurgie*, 1905, **2**, 497. [3] *Ibid.*, 503.

ORGANIC CHEMISTRY—ALIPHATIC DIVISION.

A CONSIDERABLE part of the work done in organic chemistry at the present time has for its principal object the elucidation of some problem in physical, biological, or steric chemistry, and there is every indication that chemists are taking increased advantage of biological methods and of the principles of physical chemistry in working out problems of pure organic chemistry; some of the most important recent results, indeed, owe their success to the application of such methods and principles.

Much interesting work has been done in connection with the behaviour of gases or vapours of carbon compounds under the influence of heat, of the silent discharge, and of finely divided metals. Although comparatively few papers have appeared on the chemistry of the carbohydrates, results of considerable importance have been obtained in this department. The application of Grignard's reaction shows undiminished popularity as a subject for investigation, and the researches on polypeptides continue to be actively pursued. A noteworthy coincidence is the large amount of attention which appears to have been given to aldehydes and aldehyde-acids.

Notwithstanding the exhaustive character of the researches which have been made during the last two or three years on the applications of *Grignard's reaction* in organic synthesis, a considerable number of new observations continue to be published. Many of these have reference more particularly to compounds belonging to the cyclic division, but the following may be mentioned as examples of general application of the reagent. It is shown by Tschitschibabin [1] that esters of the type RCO_2Et may be obtained by the action of magnesium alkyl haloids, RMgX, on the esters of carbonic acid. The three changes which might be expected to result from this action are the following:

1. $CO(OEt)_2 + RMgX = R{\cdot}C\leqslant^{OMgX}_{(OEt)_2}$;

2. $RC\leqslant^{OMgX}_{(OEt)_2} + RMgX = R_2C<^{OMgX}_{OEt} + MgXOEt$;

3. $R_2C<^{OMgX}_{OEt} + RMgX = R_3C{\cdot}OMgX + MgXOEt$,

[1] *Ber.*, 1905, **38**, 561.

and these products on hydrolysis would give esters, ketones, and tertiary alcohols respectively.

Experiment shows that the first of these changes is the principal one, the yield of ester on hydrolysis being in some cases as much as 80 per cent. of that required by theory.

If esters of ortho-carbonic acid are employed, the changes to be expected (from analogy with the behaviour of ortho-formic esters) are

$$C(OEt)_4 + RMgX = RC(OEt)_3 + MgXOEt$$

and

$$RC(OEt)_3 + RMgX = R_2C(OEt)_2 + MgXOEt.$$

Here again the change takes place principally according to the first type, provided the experiment is carefully conducted and the action is not too prolonged.

The replacement of aldehydic oxygen by two univalent alkyl groups has hitherto been accomplished only in an indirect way; F. and L. Sachs [1] now show that in certain cases this change can be brought about with the agency of Grignard's reaction. *p*-Dimethylamino-benzaldehyde, for example, when acted on by magnesium methyl bromide, yields first $(CH_3)_2N{\cdot}C_6H_4{\cdot}CH{<}^{CH_3}_{OMgBr}$, and this by further action of the reagent at a higher temperature gives

$$(CH_3)_2N{\cdot}C_6H_4{\cdot}CH{<}^{CH_3}_{CH_3}$$

(p-*iso*propyldimethylaniline).

It is pointed out by Beckmann [2] that *organo-calcium* haloids, analogous to the magnesium compounds, may be obtained by the action of ethyl iodide or iodobenzene on finely divided calcium. In benzene solution, negative results are obtained, even if a small quantity of ether is added, but in absolute ethereal solution the change takes place rapidly with formation of an additive compound, $CaRI,Et_2O$. Iodobenzene gives the compound PhCaI, the action taking place readily in ethereal solution if a trace of iodine is added. This compound reacts with benzaldehyde to give a product which, on hydrolysis, yields benzhydrol; when treated with carbon dioxide and the product decomposed by water, benzoic acid is obtained.

By the action of metallic magnesium on ethylene dibromide, Grignard and Tissier (1901) obtained only magnesium bromide and ethylene; but Ahrens and Stapler [3] now find that these substances react in ethereal solution to produce a crystalline compound which has the composition $CH_2Br{\cdot}CH_2{\cdot}MgBr(C_2H_5)_2O$. This product is decomposed by water, giving ethylene, ether, and magnesium bromide;

[1] *Ber.*, 1905, **38**, 517. [2] *Ibid.*, 904. [3] *Ibid.*, 1296, 3259.

when shaken with benzaldehyde in ethereal solution, it reacts in the manner of other organo-metallic haloids, giving the compound $C_6H_5\cdot CH(OMgBr)\cdot CH_2\cdot CH_2Br(C_2H_5)_2O$, and this when acted on by water produces benzaldehyde, ether, ethylene, and magnesium bromide. In both cases, therefore, the action of water yields all the bromine in the ionic condition. If a small quantity of iodine is added to the ethereal solution of ethylene dibromide, the action of magnesium gives rise to an oil which, on treatment with benzaldehyde, yields a yellowish-white powder having a composition corresponding to the formula $C_6H_5\cdot CH(OMgBr)\cdot CH_2\cdot CH_2\cdot CH(OMgBr)\cdot C_6H_5$. The authors consider that the constitution of these products is best represented on the oxonium type of Baeyer and Villiger,[1] the compound first mentioned being $\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\!\!>\!O\!<\!\!\begin{matrix}Br\\Mg\cdot CH_2\cdot CH_2Br'\end{matrix}$ and the additive compound with benzaldehyde,

$$\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\!\!>\!O\!<\!\!\begin{matrix}Br\\CH(C_6H_5)\cdot O\cdot Mg\cdot CH_2\cdot CH_2Br.\end{matrix}$$

They further show that dry bromine acts on magnesium in cold ethereal solution, giving an oily product, $\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\!\!>\!O\!<\!\!\begin{matrix}Br\\MgBr\end{matrix}$; this reacts with benzaldehyde, furfural, ethyl acetoacetate, ethyl malonate, piperidine, &c., to produce additive compounds. Iodine yields a product analogous to that given by bromine, but it is unstable.

With metallic calcium, bromine in ethereal solution yields a crystalline product of similar constitution which combines with piperidine to give an additive product.

Tschelinzeff,[2] after discussing the various views which have been put forward as to the constitution of the ether complexes formed with the magnesium organic compounds, comes also to the conclusion that the formula of Baeyer and Villiger gives the best explanation of the facts. This author has attempted to throw further light on the question, and on the oxonium bases generally, by application of thermochemical methods. Although, as found by Blaise and Grignard, it is not possible directly to separate the ether in these compounds from the organo-magnesium haloid, the converse process can now be easily studied, since the individual magnesium compounds, free from ether, can be isolated. The results obtained indicate that the thermal effect of the change $RMgX + \begin{matrix}Et\\Et\end{matrix}\!\!>\!O = \begin{matrix}Et\\Et\end{matrix}\!\!>\!O\!<\!\!\begin{matrix}MgR\\X\end{matrix}$ is always positive, amounting to about 12—13 cal. for the molecular quantities indicated, the substances experimented with being ethyl, *n*-propyl, *iso*butyl, and *iso*amyl iodides and ethyl ether.

For the purpose of synthesising certain higher alcohols, a new

[1] See *Ann. Reports*, 1904, 56. [2] *Ber.*, 1905, **38**, 3664.

method, which appears to be of general application, has been devised by Grignard;[1] it will perhaps be most easily explained by the following illustration. When glycol chlorohydrin is acted on by an organo-magnesium haloid in the cold, only the hydroxyl group is attacked, thus :

$$ClCH_2 \cdot CH_2 \cdot OH + RMgX = RH + ClCH_2 \cdot CH_2 \cdot OMgX.$$

This product may now be further acted on by another molecule of an organo-magnesium haloid in which the halogen and alkyl may either be the same as or different to those originally employed :

$$ClCH_2 \cdot CH_2 \cdot OMgX + R'MgX' = R'CH_2 \cdot CH_2 \cdot OMgX + MgX'Cl.$$

By action of water on the latter compound, the alcohol $R'CH_2 \cdot CH_2 \cdot OH$ is obtained ; in this way phenylethyl alcohol, for example, can be prepared from glycol chlorohydrin.

Paal and Weidenkaff[2] have studied the action of Grignard's reagent on certain amino-acids with the object of obtaining products which might serve for the characterisation of these acids when they arise as products of proteid hydrolysis. The aliphatic amino-acids are as a rule sparingly soluble in alcohol and easily soluble in water, and it is to be expected that the "basic" alcohols which should be formed by Grignard's reaction would exhibit solubilities of the converse order, and so be easily separated. They find that glycine ethyl ester readily reacts with magnesium phenyl bromide in ethereal solution, giving a product which, when hydrolysed with dilute hydrochloric acid, yields diphenyl together with a substance crystallising in needles, which is easily soluble in alcohol and sparingly soluble in cold water. The latter substance proves to be diphenylhydroxyethylamine,

$$OH \cdot C(C_6H_5)_2 \cdot CH_2 \cdot NH_2.$$

Sabatier and Senderens have recently published[3] a very complete summary of their exhaustive researches on the hydrogenation or decomposition of various volatile compounds under the catalytic influence of finely divided nickel and certain other metals.

The action of hydrogen on volatile carbon compounds in presence of reduced nickel at temperatures below 250° constitutes a new method of hydrogenation which is of general application, and may give results which are practically unattainable by the older methods. Ethylenic or acetylenic hydrocarbons may be converted into paraffins, aldehydes and ketones yield the corresponding primary or secondary alcohols, aliphatic nitriles and oximes give rise to amines, and various other nitrogen compounds can similarly be hydrogenated ; all such changes can, it is said,

[1] *Compt. rend.*, 1905, **141**, 44. [2] *Ber.*, 1905, **38**, 1686.
[3] *Ann. Chim. Phys.*, 1905, [viii], **4**, 319—488.

be effected more readily by this than by the older processes. Carbon monoxide and dioxide are directly hydrogenated to methane, and hydrogen can easily be added to compounds having an aromatic nucleus with production of *cyclo*hexanes, cyclic alcohols, and cyclic amines. Actions of the latter type ("special" reactions), which can be obtained only with difficulty, if at all, by older methods, may easily be brought about by the influence of nickel and to some extent of cobalt, but not by copper or platinum.

Many remarkable and important changes may also take place when the volatile compounds by themselves, without admixture with hydrogen, are subjected to the action of these metals; primary and secondary alcohols, for example, are resolved, especially in presence of copper, into free hydrogen and the corresponding aldehyde or ketone. Ethylene in presence of nickel, at about 300°, yields a mixture of hydrogen, methane, and ethane, and *cyclo*hexane gives benzene and methane.

In addition to this simple resolution, or *dédoublement* as the authors term it, condensations of various types may take place; direct polymerides may result, for example, benzene from acetylene, or condensation may occur accompanied by union with hydrogen or other of the resolution products. Thus, acetylene gives rise, in addition to other products, to a solid condensed hydrocarbon, $(C_7H_6)_n$, which the authors call "cuprene."

When acetylene mixed with hydrogen is passed over cold reduced nickel, heat is evolved and the temperature may rise as high as 150°; the acetylene entirely disappears and the product has the odour of petroleum. By using a column of nickel maintained at about 200° and allowing the operation to continue for twenty-eight hours, the authors were able to condense a yellow liquid having a beautiful fluorescence, which began to boil at 45°. In its density, composition, and all its other properties it closely resembled ordinary Pennsylvanian petroleum. By passing acetylene alone over nickel heated to 200—300°, a mixture of liquid hydrocarbons was obtained, which appeared green by diffused light and red by transmitted light. This liquid began to boil at 60—70°, and in composition and properties closely resembled Caucasian petroleum. The authors suggest, as a theory of the natural formation of petroleums, that at great depths free alkali and alkaline-earth metals may exist together with their carbides, and that by action of water these give rise respectively to hydrogen and acetylene; these gases passing over nickel, cobalt, or iron, in a state of division, at a sufficiently high temperature would behave in the manner which the above experiments indicate.

The finely divided metals which were employed in these investigations were obtained by reduction of the oxides in pure hydrogen; it is necessary, however, to pay particular attention to the temperature at

which the reduction is effected; nickel reduced from its oxide at a red heat is practically inert, whereas if prepared below 300° its activity is extreme and becomes soon exhausted; for most purposes, it is preferable to carry out the reduction at about 350°.

Attention is drawn by Collie[1] to the fact that the action of the silent electric discharge on various elements and compounds often runs parallel with that of the action of light in plants; water and carbon dioxide are decomposed, nitrogen and hydrogen combine to form ammonia, formaldehyde is produced from carbon monoxide and hydrogen, and polymerisation is induced. It has been shown further that under the influence of light hydrogen may be lost from a methylene group in certain compounds, such as alcohol, and that this hydrogen may then combine with carbonyl in carbonyl compounds (thus, benzoquinone in alcoholic solution gives rise to quinol and acetaldehyde). It appeared, therefore, to be of interest to ascertain the behaviour of ethylene—a substance most nearly allied to methylene—when mixed with carbon monoxide and subjected to the action of the silent discharge. Some of the principal results arrived at were as follows: ethylene at the ordinary temperature not only unites with carbon monoxide with production of aldehydes, &c., but also polymerises, yielding a series of complicated hydrocarbons; the chief product has a boiling point approximating to that of the hydrocarbons, $C_{10}H_{20}$; this also polymerises with loss of hydrogen, giving a substance with properties something like those of india-rubber and having a composition closely approaching $(C_5H_8)_x$. A hydrocarbon boiling at about 250° was also obtained, which may be $C_{15}H_{30}$. A remarkable similarity evidently exists between some of these products and those which are built up in a plant; the changes, moreover, can be brought about at the ordinary temperature, and, by further oxidation at the ordinary temperature, a series of aldehydes and acids can be produced.

Reference was made in the previous report to the investigations of Bone, Stockings, and Wheeler on the chemistry of combustion of methane, ethane, ethyl alcohol, acetaldehyde, and ethylene. Further experiments have since been made by Bone and Andrew[2] on the combustion of acetylene, and some of their principal results may be summarised as follows:—

The process is essentially of the same type as that involved in the cases of methane, ethane, and ethylene, the oxygen being initially incorporated with the hydrocarbon and giving rise to an unstable molecule which rapidly undergoes thermal decomposition into simpler products.

When mixtures of acetylene and oxygen are sealed up in glas

[1] *Trans.*, 1905, **87**, 1542. [2] *Ibid.*, 1232.

vessels at atmospheric temperature and pressure and then heated, they begin to interact at 250°, or sometimes below; at 300°, the change proceeds rapidly and explosive combustion takes place at about 350—375°, according to the composition of the mixtures taken. In the burning of acetylene there is no preferential oxidation of either carbon or hydrogen, nor is there any evidence of the breaking down of an unstable hydroxyacetylene into carbon and steam, as was formerly suggested by Armstrong.

In the slow combustion of acetylene, carbon monoxide and formaldehyde are produced simultaneously at an early stage of the process; these products, the authors consider, are probably due to the decomposition of an unstable initial compound, such as $C_2H_2O_2\begin{pmatrix}C\cdot OH\\ \vdots\\ C\cdot OH\end{pmatrix}$. Separation of carbon occurs in the explosive combustion of acetylene only when the reacting mixture contains more than an equivalent molecular proportion of the hydrocarbon, and is to be attributed to the secondary decomposition of the excess of acetylene. In contact with hot catalysing surfaces, such as porous porcelain, acetylene unites with steam, giving acetaldehyde; this change may take place even in presence of oxygen, and may therefore cause complications in the combustion experiments when such contact is allowed. In none of the experiments was the formation of any benzene observed.

The decomposition of formaldehyde and of acetaldehyde by heat has been studied by Bone and Smith,[1] and they show that at all temperatures between 400° and 1125° formaldehyde decomposes mainly according to the equation $H\cdot CHO = CO + H_2$. At 400° and 500°, however, this principal decomposition was accompanied by some more complex change, involving a preliminary condensation of a portion of the vapour. Acetaldehyde decomposes at 400° into methane and carbon monoxide, but at 600° notable quantities of free hydrogen were obtained and some carbon deposited, although the authors have previously shown that methane does not decompose below 800°. At 800°, the proportion of hydrogen is increased, and some acetylene could also be detected in the products. In contact with porous porcelain at 450—500°, not only is carbon separated, but ethane and carbon monoxide are also produced together with crotonaldehyde, &c.

The fact that formaldehyde may be synthetically formed from mixtures of carbon monoxide or dioxide with hydrogen under the influence of the silent discharge has been fully established by earlier investigations, and more recently it has been shown by Jahn and by Bach that similar changes may be effected by means of hydrogenated palladium. With the object of throwing further light on the conditions which determine the production of formaldehyde, Chapman and Holt[2]

[1] *Trans.*, 1905, **87**, 910. [2] *Ibid.*, 916.

have subjected various gaseous mixtures to a high temperature by means of an incandescent platinum wire, and their experiments establish the fact that in the system containing carbon monoxide, carbon dioxide, steam, and hydrogen, formaldehyde is undoubtedly produced.

Interesting studies on the condition of formaldehyde in aqueous solution have been made by Auerbach and Barschall.[1] The pure aldehyde was obtained by subliming trioxymethylene in a stream of nitrogen, and its strength was estimated by the sulphite method of Lumière and Seyewetz or by Romijn's iodine method. Determinations of the molecular weight in the cryoscopic way indicated that the value depends on the concentration of the solution. By application of the law of mass action to the values so obtained, it is shown that a state of reversible equilibrium probably exists between the single and the trimeric forms, the same limit being reached under the same conditions whether gaseous formaldehyde or solid paraformaldehyde is employed. There are some indications that in strong solutions polymerides higher than $(CH_2O)_3$ may exist. Rise of temperature causes a displacement of the equilibrium in the direction of increase in the proportion of the single or unimolecular form, the polymeric forms being decomposed with absorption of heat.

The authors find that when an aqueous solution of formaldehyde is distilled, the distillate is always poorer and the residue richer in formaldehyde than the original solution. It is probable that when gaseous formaldehyde is dissolved in water only a small part exists in the original condition, the greater part being converted into hydrated or polymerised forms.

A knowledge of the behaviour of formaldehyde in dilute alkaline solution is a matter of considerable importance in throwing light on the function of alkalis in bringing about the condensation of formaldehyde to sugars, and an investigation in this direction has been undertaken by H. and A. Euler.[2] These authors come to the conclusion that formaldehyde behaves itself as a weak acid, the salts formed with strong bases being considerably hydrolysed in aqueous solution. They calculate that in a normal solution of the monosodium derivative about one-half exists as such, the remainder being hydrolysed to free base and formaldehyde. In dilute aqueous solution the "salt" behaves as a binary electrolyte, the change being probably represented by the relation:

$$HC\langle^{OH}_{OH} + \overset{+}{N}a + \overset{-}{O}H = \overset{-}{H}C\langle^{O}_{OH} + \overset{+}{N}a + H_2O.$$

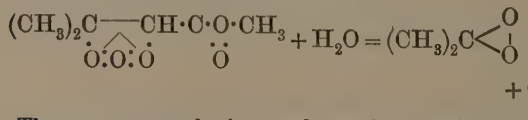
[1] *Arbb. Kais. Ges.*, *A*, **22**, 584; from *Chem. Centr.*, 1905, ii, 1081.
[2] *Ber.*, 1905, **38**, 2551.

The change which formaldehyde undergoes in contact with bases is made up of two independent parts, the condensation and the formation of formates and methyl alcohol. The latter change has also been investigated by the authors, and they show that production of sodium or barium formate by the action of the hydroxides on formaldehyde is a reaction of the second order; with great excess of the aldehyde, it behaves as a reaction of the first order, the concentration of the aldehyde being then practically constant. Calcium hydroxide behaves abnormally in the latter respect, and the authors suggest that a calcium-formaldehyde complex is formed in this case; it appears that this result has an important bearing on the observation of Loew (1888) that calcium hydroxide acts much better than barium hydroxide as a condensing agent of formaldehyde to sugars. It is evident from the authors' results that the activity of different bases in bringing about the sugar condensation does not stand in direct relation to their reaction velocity in the production of formates.

In a subsequent communication,[1] Auerbach takes exception to some of the results of the last named authors. He considers that it is not possible that their formaldehyde could have been free from methyl alcohol, since they prepared it from commercial formol by distillation (after dilution and neutralisation). The strength of their solution, moreover, was determined by the cryoscopic method, which, in view of the above-mentioned observations of Auerbach and Barschall, would give misleading results.

Pyruvic aldehyde or *methylglyoxal* was first obtained by Pechmann in 1887; *iso*nitrosoacetone was acted on by a 30 per cent. solution of sodium hydrogen sulphite and the resulting crystalline compound was decomposed with dilute acids. In this way a product was obtained which was volatile in steam and which was recognised as methylglyoxal by its reactions with ammoniacal silver solution, Schiff's reagent, tolylenediamine, and phenylhydrazine, the latter yielding the dihydrazone, $CH_3 \cdot C(:N_2HPh) \cdot CH:N_2HPh$, melting at 145°. This aldehyde has now been prepared by Harries and Türk [2] in an entirely different way, as follows.

Mesityl oxide when treated with ozone in the cold yields the ozonide, $C_6H_{10}O_5$, as a green, explosive syrup. When a solution of this compound is warmed, it yields white crystals of acetone peroxide, and the solution contains methylglyoxal:



$$+ CH_3 \cdot CO \cdot CHO + H_2O_2.$$

The aqueous solution reduces Fehling's solution in the cold and

[1] *Ber.*, 1905, **38**, 2833. [2] *Ibid.*, 1630.

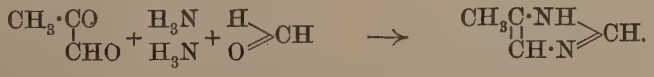
yields with phenylhydrazine the dihydrazone referred to above. When distilled in a vacuum, a considerable part of the aldehyde passes over, and this watery distillate, when again carefully evaporated, leaves a nearly colourless liquid which sets to a glassy mass when kept over sulphuric acid. Analysis and molecular weight determination show that the latter product is a polymeride of methylglyoxal having the formula $(C_3H_4O_2)_4$.

The di-semicarbazone and the mono-acetal of methylglyoxal were also isolated, and hydroxylamine yielded the dioxime (methylglyoxime) identical with the product prepared from *iso*nitrosoacetone by V. Meyer in 1882.

Since dextrose under the influence of dilute alkalis is known to undergo various transformations leading to the production of hydroxy-acids, such as lactic acid, it might be expected that in presence of ammonia analogous changes would occur resulting in the formation of alanine or other amino-acids of similar type. Windaus and Knoop,[1] while working in this direction, have observed that ammonia itself acts only very slowly on dextrose, but that by employing, instead of ammonia, the strongly dissociated "zinc hydroxide-ammonia," reaction takes place, even in the cold, with production of an oxygen-free base; the latter, which is formed in considerable quantity, proves to be methylglyoxaline or methyliminazole (either the α- or the β-derivative).

This result has an important bearing on the question as to the nature of the intermediate products which are formed in the transition of dextrose to lactic acid. It was suggested by Pinkus that the formation of acetol is the intermediate stage, whilst the work of Nef, Wohl, and Buchner gives support to the view that glyceraldehyde is first formed and that this passes, by loss of water, to methylglyoxal; by again assimilating the elements of water, the latter gives rise to lactic acid.

The latter view, namely, that methylglyoxal is formed, appears to be favoured by the results here mentioned, since glyoxalines are known to be produced by condensation of orthodicarbonyl compounds with formaldehyde and ammonia. The authors consider that the methylglyoxaline arises in this way in the present case, the change being expressed as follows:



The formaldehyde necessary for this reaction may arise, it is suggested, as a primary reversible degradation product of the hexose, or

[1] *Ber.*, 1905, **38**, 1166.

possibly it may have its origin in the decomposition of methylglyoxal. The yield of pure methylglyoxaline from 1 kilogram of dextrose is about 100 grams.

Buchner and Meisenheimer,[1] in discussing the formation of lactic acid from dextrose and of alcohol from lactic acid, favour the opinion that methylglyoxal is produced as an intermediate stage in the fermentation of sugar to lactic acid, and they show that this assumption is in accord with the fact that only the inactive acid is obtained, whether cane sugar or dextrose is started with.[2] That alcohol may be produced from lactic acid by fermentation has been shown by Fitz (1880) and Maze (1902). Duclaux in 1886 observed that calcium lactate in presence of air and sunlight gave rise to alcohol, calcium carbonate, and calcium acetate, and Hanriot (1886) obtained considerable quantities of alcohol by heating calcium lactate with lime. The authors confirm the latter observation, but they show that the distillate, which was regarded by Hanriot as ethyl alcohol, contains also *iso*propyl alcohol. Incidentally, they have also proved that ethyl alcohol is formed, although only in small quantity, when invert sugar is heated with a strong solution of sodium hydroxide.

Although on the whole there is much evidence in favour of the hypothesis that lactic acid may play an important part as an intermediate stage in the alcoholic fermentation of sugar, it must be remarked that the recent experiments of Slator[3] appear to indicate that "it is improbable that any but small quantities of sugar go through the intermediate step of lactic acid in fermentation."

Maleic Semi-aldehyde.—By the oxidation of pyromucic acid with bromine in aqueous solution, Limpricht in 1873 obtained this substance as an indistinctly crystallisable oil, but its properties were but little studied. Fecht[4] has now improved the method of preparation and made a further study of the compound. Pyromucic acid is oxidised with potassium hypobromite, and the solution, after saturation with sodium sulphate, is extracted many times with ether. The product thus obtained is dried in a vacuum at 80°, and the crystalline mass resulting is distilled under a pressure of 0·1 to 0·3 mm. After crystallisation from ether and benzene, the semi-aldehyde is obtained in the form of flat needles, which melt at 55° and boil at 145° under 10 mm. pressure with slight decomposition.

Phenylhydrazine acetate in the cold gives a yellow, crystalline hydrazone (m. p. 158°), and a white, crystalline oxime is obtained by the action of hydroxylamine hydrochloride in acid solution. On

[1] *Ber.*, 1905, **38**, 620.
[2] Compare, however, McKenzie, *Trans.*, 1905, **87**, 1379.
[3] *Proc.*, 1905, **21**, 304.
[4] *Ber.*, 1905, **38**, 1272.

saturating a solution of the oxime in methyl alcohol with hydrogen chloride in the cold, a large yield of methyl fumarate is obtained, this result being due to the Beckmann rearrangement.

When the semi-aldehyde is neutralised with sodium bicarbonate and heated with potassium cyanide on the water-bath, it is transformed almost quantitatively into succinic acid.

Maleic Dialdehyde.—Marquis in 1901 observed that when furfuran is nitrated in acetic anhydride solution below $-5°$, the product treated with water and extracted with ether, an oil is obtained which has reducing properties and which reacts with phenylhydrazine to give a crystalline hydrazone melting at 230°. This reducing substance appears to be nitrosuccinaldehyde monacetin, $CHO{\cdot}CH(NO_2){\cdot}CH{:}CAc{\cdot}OH$. When the latter is boiled with water, it yields an aldehyde, the phenylhydrazone of which contains no oxygen. The author now shows[1] that this is the *dialdehyde of maleic acid*, $CHO{\cdot}CH{:}CH{\cdot}CHO$; with hydroxylamine, it reacts to produce the dioxime, $\begin{matrix} CH{\cdot}CH{:}NOH \\ | \\ CH{\cdot}CH{:}NOH \end{matrix}$.

Tartronic Semi-aldehyde.—From the product of the action of an aqueous solution of caustic soda on an ether-alcohol solution of collodion-wool, W. Will in 1891 obtained an acid which has powerful reducing properties, and which with phenylhydrazine acetate gives the osazone $CH(:N_2HPh){\cdot}C(:N_2HPh){\cdot}CO_2H$. This osazone was previously obtained by Nastvogel by the action of phenylhydrazine on dibromopyruvic acid, and it may be regarded either as the dihydrazone of mesoxalic semi-aldehyde, or as the osazone of tartronic semi-aldehyde or of hydroxypyruvic acid. Analysis of the calcium, strontium, and cadmium salts of Will's acid indicated the formula $C_3H_4O_4$ for the free acid, so that it must be either tartronic semi-aldehyde, $CHO{\cdot}CH(OH){\cdot}CO_2H$, or hydroxypyruvic acid,

$$CH_2(OH){\cdot}CO{\cdot}CO_2H.$$

Since the acid is stable towards bromine water and towards alkalis, such as barium hydroxide, Will concluded that it was the keto- and not the aldehyde-acid. Aqueous solutions of the acid, or its salts, were found to be feebly lævorotatory, and this circumstance was at the time supposed to lend further support to the ketonic formula, attention being drawn to the presence of the $-CO{\cdot}CH_2{\cdot}OH$ group in lævulose.

Since, however, in the constitution of hydroxypyruvic acid there is no asymmetric carbon atom, it was evident that the matter required further investigation. This was undertaken by Aberson,[2] who states that by repeated evaporation of the solution of Will's acid the optical activity diminishes and finally disappears, although in other respects

[1] *Ann. Chim. Phys.*, 1905, [viii], **4**, 196.

[2] *Zeit. physikal. Chem.*, 1899, **31**, 17.

the properties remain unaltered. He concludes therefore that the optical activity was due to some impurity containing nitrogen, since traces of oxides of nitrogen can be detected in the process of evaporation.

By heating this inactive acid in sealed tubes with hydrocyanic acid, Aberson obtained a product which, on treatment with hydrochloric acid and then with barium hydroxide, gave rise to barium glycerate; the latter he assumes must result from the decomposition of *iso*tartaric acid, $CH_2(OH)\cdot C(OH)(CO_2H)_2$, and considers that this fact establishes the ketonic acid formula for Will's acid, since the aldehydic acid would under similar treatment yield tartaric acid.

Neuberg and Silbermann[1] have now made a further study of this product and they arrive at a conclusion different from that of Aberson; the work of the latter chemist appears, moreover, to have been overlooked. Their results may briefly be summarised as follows: Will's product was obtained in the manner above indicated, the acid being precipitated in the form of lead salt and the latter decomposed by hydrogen sulphide. The acid solution so prepared was feebly lævorotatory, powerfully reducing, gave precipitates with baryta water and with ammoniacal calcium chloride, and with phenyl hydrazine yielded Nastvogel's osazone. In addition to these properties, they find that the acid yields a characteristic *brucine* salt which crystallises in needles.

By acting on a solution of the active acid with excess of potassium cyanide and hydrolysis of the resulting product, an acid was isolated (by means of its lead salt and acid potassium salt) which proved to be *l-tartaric acid*, mesotartaric acid being probably simultaneously formed. From this result, the authors conclude that Will's acid is in reality not hydroxypyruvic acid, but the semialdehyde of tartronic acid or, as they term it, aldehydo-glyceric acid. The configuration of this acid must evidently be $\begin{matrix}\mathrm{CHO}\\ \mathrm{HC}\cdot\mathrm{OH}\\ \mathrm{CO_2H}\end{matrix}$, *l*-tartaric acid being

$$\begin{matrix}\mathrm{CO_2H}\\ \mathrm{OHCH}\\ \mathrm{HC}\cdot\mathrm{OH}\\ \mathrm{CO_2H}\end{matrix}.$$

Reduction of the aldehyde-acid with sodium amalgam is shown to give rise to *l*-glyceric acid, from which it follows that the configuration $\begin{matrix}\mathrm{CH_2}\cdot\mathrm{OH}\\ \mathrm{HC}\cdot\mathrm{OH}\\ \mathrm{CO_2H}\end{matrix}$ is to be assigned to the latter.

[1] *Zeit. physiol. Chem.*, 1905, **44**, 134.

The above changes therefore, in the author's opinion, represent a transformation from the *d*- to the *l*-series, since cellulose, from its relation to *d*-glucose, must be regarded as belonging to the former.

In connection with the question as to the constitution of Will's acid, it may be mentioned that when glyceric acid is oxidised in presence of iron, a product is obtained which, with phenylhydrazine, yields Nastvogel's osazone.[1] This differs from Will's acid in that it gives an intense violet colour with ferric salts in presence of alkali and must be either hydroxypyruvic or dihydroxyacrylic acid.

Mesoxalic semi-aldehyde has been further studied by the writer.[2] It is easily prepared by the action of mercuric chloride on dihydroxymaleic acid and is fairly stable in acid solution; alkalis transform it to tartronic acid. When heated for some time, it yields glyoxal, and with urea it condenses with evolution of carbon dioxide, giving glycoluril.

Mesoxalic dialdehyde has hitherto been known only in the form of its oxime (di*iso*nitrosoacetone) and its di- and tri-phenylhydrazides. Harries and Türk[3] have recently succeeded in obtaining the free aldehyde in the following way. Crystallised phorone when dissolved in chloroform and treated with ozone yields a diozonide, $C_9H_{14}O_7$, as a green, explosive syrup; on shaking this with ice-water, it slowly decomposes and crystals of acetone peroxide slowly separate. The clear solution which remains after separation of the latter substance, when concentrated under reduced pressure, yields a viscid syrup which sets to a glassy mass if dried in a vacuum desiccator; analysis shows this to be a hydrate of mesoxalic dialdehyde. The water may be removed by heating for some time to 65° over phosphoric oxide, and a yellow, brittle mass is then obtained which has the composition of the anhydrous dialdehyde, but which is doubtless a polymeric form. The monomeric form is volatile in steam and the distillate gives with phenylhydrazine acetate the triphenylhydrazide,

$$C(N_2HPh):(CHN_2HPh)_2,$$

which was previously obtained by Pechmann and Jenisch in 1891 from acetonedicarboxylic acid and diazobenzene chloride.

The authors explain the formation of the dialdehyde and acetone peroxide from phorone diozonide as follows:

$$(CH_3)_2C(O{:}O{:}O)CH\cdot CO\cdot HC(O{:}O{:}O)C(CH_3)_2 = 2(CH_3)_2C{<}\begin{matrix}O\\|\\O\end{matrix} + CHO\cdot CO\cdot CHO.$$

Henle and Schupp[4] have obtained an aqueous solution of mesoxalic dialdehyde by acting with nitrous acid on an ice-cold aqueous solution

[1] Fenton and Jones, *Trans.*, 1900, **77**, 73.
[2] *Trans.*, 1905, **87**, 813.
[3] *Ber.*, 1905, **38**, 1630.
[4] *Ibid.*, 1372.

of Pechmann's di*iso*nitrosoacetone, the process being analogous to that by which Harries obtained succinic dialdehyde from the corresponding dioxime :

$$OH{\cdot}N{:}CH{\cdot}CO{\cdot}CH{:}N{\cdot}OH + 2HO{\cdot}NO = OCH{\cdot}CO{\cdot}CHO + 2H_2O + 2N_2O.$$

By action of phenylhydrazine acetate in the cold, this product yielded the bisphenylhydrazone of mesoxalic dialdehyde (or its isomeride) melting at 176°.[1]

Lævulic aldehyde was obtained by Harries in 1898 from α-dimethylfurfuran; when this is acted on by hydrogen chloride in methylalcoholic solution, lævulinmethylal, $CH_3{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CH(OMe)_2$, is produced, and this, by action of dilute hydrochloric acid, is readily hydrolysed to the aldehyde. The same author has now [2] succeeded in obtaining this aldehyde in an entirely different way, which is of much interest from a general standpoint. When Para caoutchouc is dissolved in chloroform and treated with ozonised oxygen, a viscid oil is obtained which, after standing in a vacuum desiccator, sets to an explosive, glassy mass. Analysis and molecular weight determinations of this ozonide show that it has the formula $C_{10}H_{16}O_6$. If this product is treated with water and distilled in steam, lævulic aldehyde passes over, and may be recognised by its reducing properties and behaviour with phenylhydrazine and hydroxylamine. If the action of steam is continued for a short time only and the solution cooled, crystals separate which prove to be lævulic aldehyde peroxide. The decomposition of the ozonide may therefore be represented by the relation :

$$C_{10}H_{16}O_6 = \begin{matrix} O{:}C(CH_3){\cdot}CH_2{\cdot}CH_2{\cdot}CH{:}O \\ \| \qquad\qquad\qquad\qquad\qquad\qquad \| \\ O{=}\!\!=\!\!=\!\!=

An experimental connection is seen in the fact that α-dimethylfurfuran was isolated by the author from beech wood tar and that a mixture of methylated furfurans was obtained by Fischer and Laycock (1889) from the dry distillation of sugar with lime. Lævulic aldehyde, as above shown, results by simple processes of treatment both from caoutchouc and from dimethylfurfuran; the connection between lævulic acid and the carbohydrates is, of course, well known.

It is pointed out by Winkler[1] that the commercial "absolute" ethyl alcohol not only contains from 1 to 2 per cent. of water, but is usually contaminated also with some aldehyde. The ordinary process of fractional distillation and purification with lime, barium oxide, or sodium does not yield a product free from aldehyde, and for purposes in which the perfectly pure substance is requisite, as in absorptiometric investigations, the author recommends the removal of the aldehyde by silver oxide and caustic alkali and subsequent dehydration by metallic calcium.

It would appear from the author's observations that the usual statements as to the extremely hygroscopic nature of absolute alcohol are somewhat exaggerated; less than 0·1 per cent. of water was absorbed by 200 c.c. of absolute alcohol when exposed in an open vessel for fifteen minutes.

Mathieu[2] points out that aldehyde is formed in wines and other alcoholic liquids by simple contact with air at the ordinary temperature, even without the influence of micro-organisms or porous substances. The oxidation is favoured by the presence of oxidisable substances and by sunlight.

For the identification of minute quantities of ethyl alcohol, Buchner and Meisenheimer[3] employ *p*-nitrobenzoyl chloride, which gives a quantitative yield of crystalline ethyl *p*-nitrobenzoate melting at 57°.

Sabatier and Senderens[4] employ the method of decomposition in presence of metallic copper, which was referred to on p. 70, for the distinction between primary, secondary, and tertiary alcohols; in the product, they identify aldehydes by Schiff's reagent and ketones by semicarbazide; the olefinic hydrocarbons obtained from tertiary alcohols are recognised by the property of decolorising bromine.

Weinland and Schmid[5] draw attention to the fact that alkyl haloids may readily be obtained by the action of methyl or ethyl sulphate on a metallic haloid in aqueous solution. When, for example, potassium

[1] *Ber.*, 1905, **38**, 3612.
[2] *Bull. Assoc. Chim. Sucr. Dist.*, 1905, **22**, 1283.
[3] *Ber.*, 1905, **38**, 625.
[4] *Bull. Soc. chim.*, 1905, [iii], **33**, 263.
[5] *Ber.*, 1905, **38**, 2327.

iodide is dissolved in its own weight of water and gently warmed with methyl sulphate in calculated quantity, a nearly theoretical yield of pure methyl iodide is obtained. In the dry state, potassium chloride and potassium methyl sulphate yield methyl chloride, and methyl bromide is also formed, mixed with other products, in a similar way from metallic bromides. Methyl iodide cannot be prepared in this dry way since large quantities of iodine vapour result. It appears[1] that Dumas in 1835 prepared methyl chloride by heating dry sodium chloride with methyl sulphate, but the fact appears to have escaped notice.

Methylazoimide, $(CH_3)N_3$, has been obtained by Dimroth and Wislicenus[2] as a colourless liquid boiling at 20°, which explodes only if heated above 500°. It is prepared by acting on an aqueous solution of sodium azoimide with methyl sulphate.

In preparing alkyl iodides from alcohols by means of iodine and phosphorus, it is often assumed that the proportion of the two latter substances should be that corresponding to the tri-iodide, but it is found by Walker and Johnson[3] that by using the proportion corresponding to the penta-iodide a yield of 87 per cent. or more of the theoretical quantity of methyl iodide may be obtained.

Bogojawlensky and Narbutt[4] have studied the influence of various water-absorbing metallic salts on the esterification of ethyl alcohol with various organic acids. They show, for example, that potassium pyrosulphate increases the yield of ester in the case of both aliphatic and aromatic acids, but the influence of copper sulphate appears to be favourable only as regards aliphatic acids unless a little free sulphuric acid is also present; the latter appears to exert a good influence in nearly all cases.

For the purpose of removing the water formed during the preparation of esters, Taylor[5] makes use of the principle described by Young,[6] namely, the addition of benzene and distillation of the more volatile ternary mixture—alcohol, benzene, water.

Sudborough and Thomas[7] describe a simple method for the estimation of acetyl groups, which consists in hydrolysing the compound with either benzenesulphonic acid or with naphthalene-α- or -β-sulphonic acid and distilling off the resulting acetic acid in steam. The distillate is then titrated with barium hydroxide, using phenolphthalein as indicator. The acids mentioned have the advantage over phosphoric acid that they are relatively stronger and, unlike sulphuric acid, they have no tendency to yield acid gases such as sulphur dioxide.

[1] *Loc. cit.*, p. 3696.
[2] *Ber.*, 1905, **38**, 1573.
[3] *Trans.*, 1905, **87**, 1596.
[4] *Ber.*, 1905, **38**, 3344.
[5] *Proc. Roy. Soc. Edin.*, 1905, **25**, 831.
[6] *Trans.*, 1902, **81**, 709.
[7] *Ibid.*, 1905, **87**, 1752.

The ordinary methods available for bringing about the replacement of hydroxyl by bromine, such as the action of hydrobromic acid or of phosphorus bromides, may often lead to very unsatisfactory results, especially in the case of aliphatic polyhydric compounds such as glycerol, erythritol, and mannitol. Perkin and Simonsen [1] have now pointed out that the process may be greatly improved if the hydroxy-groups are first acetylated and the resulting acetate is then treated with hydrogen bromide in glacial acetic acid at 150°. In this way, it is generally possible to substitute all the hydroxy-groups by bromine, and the process goes on smoothly without danger of carbonisation, &c. Glycol diacetate and glyceryl triacetate give in this way quantitative yields of ethylene dibromide and *s*-tribromopropane. Erythritol tetracetate yields *s*-tetrabromobutane (two modifications) and erythritol tribromohydrin. The tetracetate of penterythritol, $C(CH_2{\cdot}O{\cdot}CH_3{\cdot}CO)_4$, treated in a similar way at 160°, gave *s*-tetrabromotetramethylmethane, $C(CH_2Br)_4$, together with the acetyltribromo-derivative, $(CH_2Br)_3C{\cdot}CH_2{\cdot}O{\cdot}CO{\cdot}CH_3$. Mannitol hexacetate gave only the acetylpentabromo-derivative, $C_6H_8Br_5(O{\cdot}CO{\cdot}CH_3)$, the sixth acetyl group obstinately resisting replacement.

The synthetical preparation of glycerides of the higher fatty acids has hitherto been effected by the direct esterification of glycerol with the free acid (Berthelot) or by the action of chlorohydrins with salts of the acid. Grün [2] finds that in many cases it is advantageous to start with the sulphuric ester of glycerol or of the chlorohydrin and to act on this with a solution of the fatty acid in concentrated sulphuric acid. When glycerol is esterified with sulphuric acid, the action stops at the stage of the disulphate, even if great excess of acid is used, and the action of the fatty acids on this product yields only diglycerides under the conditions stated. In this reaction, apparently the two primary alcoholic groups undergo esterification, so that $\alpha\alpha$-diglycerides result. Starting, however, with glycerol α-chlorohydrin, the primary and secondary group are esterified and $\alpha\beta$-diglycerides are obtained.

If the hydroxyl or halogen in these compounds is replaced by acid radicles which are different from those already contained in the diglyceride, it is possible to prepare the structurally isomeric pairs of symmetrical and unsymmetrical triglycerides,

$CH_2(O{\cdot}COR){\cdot}CH(O{\cdot}COR'){\cdot}CH_2{\cdot}O{\cdot}COR$ and

$CH_2(O{\cdot}COR){\cdot}CH(O{\cdot}COR){\cdot}CH_2{\cdot}O{\cdot}COR'$,

and it should evidently be possible to resolve the latter into its optically active components.

In the previous report, attention was drawn to the interesting work of Votoček and Vondráček on the separation of certain sugars in

[1] *Trans.*, 1905, **87**, 855. [2] *Ber.*, 1905, **38**, 2284.

a mixture by successive treatment with different hydrazines. These authors show further [1] that by the action of a suitably chosen hydrazine on the hydrazone of a sugar it is possible to effect an interchange of hydrazine-residues in the sense $AB_1 + B_2 = AB_2 + B_1$, provided the newly formed hydrazone has a smaller solubility. Similarly, one sugar may replace another from its hydrazone, provided the resulting hydrazone is less soluble than the one acted on; it is also possible to bring about "double decomposition" between two sugar hydrazones with the production of that which is less soluble. These reactions, which resemble to some extent the behaviour of salts in solution, suggest the hypothesis that a certain amount of dissociation takes place when a sugar hydrazone is dissolved. Galactosephenylhydrazone, for example, reacts with mannose, giving mannosephenylhydrazone, galactose being liberated. The phenylmethylhydrazone of dextrose behaves similarly towards galactose, and the diphenylhydrazone of dextrose towards arabinose. Double decomposition occurs between galactosephenylhydrazone and dextrosephenylmethylhydrazone. These replacements take place in water or dilute alcoholic solutions, and are accelerated by slight acidification with acetic acid. In the case of the diphenylhydrazones, the change occurs only if acetic acid is present.

Dierssen in 1903 observed that when starch is hydrolysed by means of oxalic acid there is formed, in addition to dextrose, a disaccharide apparently identical with Lintner's *iso*maltose and lævulose. The latter, according to Ost,[2] is not a primary product of the hydrolysis, but arises owing to the action of the acid on dextrose. By dissolving dextrose in a mixture of equal volumes of strong sulphuric acid and water and allowing the mixture to stand for four months at the ordinary temperature, the author obtained from 5 to 10 per cent. of lævulose.[3]

The author discusses some of the methods of detecting lævulose in mixtures and gives preference to that of Dubrunfaut, namely, the separation as calcium lævulosate.

As a delicate test for lævulose, Pinoff [4] recommends heating the solution with a mixture of ammonium molybdate and a little acetic acid to 95°. After three minutes, lævulose produces a beautiful blue colour, whereas with other sugars the solution remains colourless during this period. When the heating is continued for half an hour, arabinose, rhamnose, galactose, mannose, and sorbose produce a feeble green colour, but no blue. Mineral acids must be absent,

[1] *Ber.*, 1905, **38**, 1093.
[2] *Zeit. angew. Chem.*, 1905, **18**, 1170.
[3] Compare Fenton and Gostling, *Trans.*, 1901, **79**, 363.
[4] *Ber.*, 1905, **38**, 3317.

otherwise most sugars will give a blue colour under the above conditions.

The same author has made a further study of various other colour reactions for carbohydrates, such as Tollen's phloroglucinol reaction for pentoses and Molisch's α-naphthol reaction, especially with the object of ascertaining the influence of conditions on the character of the absorption bands given by the coloured solutions produced.

A colour-reaction of lactose which distinguishes it from other carbohydrates, and which may be used to detect it in mixtures, is given by Graaff.[1] The substance is heated with diphenylhydrazine and acetic acid, when, if lactose is present, the original brownish-violet colour of the mixture changes eventually to blackish-green and finally brown. If 70 per cent. alcohol is added at the green stage, a characteristic green solution is obtained. The green colouring matter dissolves also in ether or chloroform.

Van Ekenstein and Blanksma[2] recommend an alcoholic solution of *p*-nitrophenylhydrazine for the separation of cane sugar from dextrose, lævulose, and mannose; these hexoses form hydrazones which are nearly insoluble in water, whereas cane sugar does not react in alcoholic solution. The same reagent may be used for the determination of many aldehydes and ketones, the yield of hydrazone being almost quantitative. *o*-Nitrophenylhydrazine behaves similarly and may be used for the separation of dextrose from lævulose, the hydrazone of the latter separating more readily from an alcoholic solution.

The compounds first observed by Morrell, which are formed by certain sugars with guanidine, have been further studied by Morrell and Bellars.[3] These compounds, which are hygroscopic, crystalline substances, are precipitated when alcoholic solutions of guanidine and the sugar are mixed together. They have a strongly alkaline reaction in aqueous solution, and their optical activity is generally much lower than that of the parent sugar. The rotation angle of the glucose compound in water in time becomes negative, and that of fructose falls to a constant value which is of the same sign as that of the parent sugar. These changes may perhaps indicate a slow transformation of glucose into fructose, like that which was observed by Lobry de Brüyn in the action of alkalis. These compounds are decomposed by the action of dilute acids, but in some cases the extent of the change is largely dependent on conditions, such as time and concentration.

Experiments of very considerable interest have been carried out by

[1] *Pharm. Weekblad*, 1905, **42**, 685.
[2] *Rec. Trav. chim.*, 1905, **24**, 33.
[3] *Proc. Camb. Phil. Soc.*, 1905, [xiii], **2**, 79.

E. F. Armstrong [1] with the view of ascertaining the manner in which the activity of various organisms which give rise to alcoholic fermentation is dependent on, or influenced by, the enzymes which they contain. About twenty selected yeasts were employed and their action was studied on four hexoses—glucose, fructose, mannose, and galactose—and on the bioses—cane sugar, maltose, and lactose. The results showed that glucose, fructose, and mannose could be fermented by all the yeasts employed, but that several of these were unable to ferment galactose. This power of a yeast to ferment glucose, &c., or its inability to ferment galactose does not depend in any way on the presence or absence of a particular sucroclastic enzyme; the author is of opinion, in fact, that the occurrence of alcoholic fermentation is altogether independent of a particular enzyme, whether free or fixed, which is able to induce the hydrolysis of either maltose or cane sugar.

The three hexoses which behave alike have already been shown to have one common enolic form, and the author considers that the formation of the enol is the initial stage in the fermentation of the hexoses, and that the breakdown of the molecule commences at the terminal carbon atom. Compounds which differ from glucose only in the groups attached to the terminal carbon atom (methyl glucosides, gluconic acid, &c.) are unfermentable.

The conception of reversible hydrolysis of the bioses or disaccharides under the influence of enzymes was first indicated by the researches of Croft Hill in 1898. Since that time, many further investigations have been made on the subject, but it is pointed out by E. F. Armstrong [2] that little has been done to advance any theory of the process or to arrive at any definite understanding as to the limitations of the changes involved. Similar remarks apply also to the action of acids which can likewise act reversibly under certain conditions.

The key to the interpretation of these changes must, in this author's opinion, be looked for in the behaviour of glucose itself in solution. The fact that glucose exists in more than one form was first clearly pointed out by Tanret in 1895; he then assumed that three forms exist, but in view of later investigations the number is now admittedly reduced to two. These two forms can be completely converted one into the other in the solid state; as crystallised from alcohol, glucose consists almost entirely of the α-form, but by heating this for several days to 105° it is changed to the β-form.[3] When either form is dissolved in water (or other solvents), partial transformation into the other form takes place until equilibrium is established, the proportions depending on the concentration and temperature.

[1] *Proc. Roy. Soc.*, 1905, **76**, 600. [2] *Ibid.*, 592.
[3] Tanret, *Bull. Soc. chim.*, 1905, **33**, 337.

The process by which a monose is converted into a biose must be regarded as precisely similar to that by which α- and β-glucoses are converted into the respective methyl glucosides; maltose must, in fact, be regarded as glucose α-glucoside and *iso*maltose as glucose β-glucoside. One would expect then that when glucose undergoes condensation to the biose form it should, if the process is uncontrolled, give rise to both maltose and *iso*maltose in proportions depending on their relative stability under the conditions.

It is shown that when the condensation of glucose is effected by acids, both maltose and *iso*maltose are formed. But since hydrolysis under the influence of enzymes is a selective process, being so controlled that it takes place in one direction only (thus, only derivatives of α-glucose are hydrolysed by maltase), it might be supposed that the tendency would be for the enzyme to reproduce that biose which it hydrolyses. As a matter of fact, the main product is a biose, *iso*-maltose, isomeric with that normally hydrolysed, and it is uncertain at present whether the normal biose, maltose, is produced at all by the action of maltase. The formation under the influence of an enzyme of a single biose which is isomeric with that which it hydrolyses could be accounted for if it is assumed that both are initially produced, but that one is again hydrolysed as fast as formed, and so all but disappears. If, however, it were shown that only the stereoisomeride of the biose hydrolysed is produced initially, it would be necessary to regard the synthetical activity of the enzyme as opposed to its hydrolytic activity. An explanation which, in a measure, unites both points of view is that the enzyme acts throughout by protecting one or the other position according as it belongs either to the α- or to the β-class of hydrolysts, thereby practically preventing condensation from taking place in more than one direction.

The author's results show that, under the given conditions, both maltose and *iso*maltose are producible from glucose, the former by the aid of the β-enzyme, emulsin, and the latter by the α-enzyme, maltase. So far it is left undecided whether maltase can give rise to maltose, but experiments are mentioned which at any rate render it probable that emulsin does not give rise to *iso*maltose.

The stereoisomeric glucosides are now of considerable importance as test materials in the study of enzyme action, and an improved method for their preparation has been published by E. F. Armstrong and Courtauld.[1] When solid anhydrous glucose is dissolved in methyl alcohol containing hydrogen chloride, it is quickly converted into a mixture of nearly equal parts of α- and β-glucoses, which then undergo etherification yielding the corresponding glucosides. If the solution is neutralised before the further slow conversion of β-methylglucoside

[1] *Phys. Proc.* 1905, July 1.

into the more stable α-form can take place and the solvent is removed, a mixture of the two forms is obtained; by subjecting this mixture to a suitably active yeast, the α-form undergoes fermentation, and the β-compound is obtained in a pure state. In this way, about 230 grams of β-methylglucoside may be obtained from 500 grams of glucose.

Maquenne[1] prepares β-methylglucoside by the action of methyl sulphate on glucose in presence of caustic potash; the α-modification is not produced under the conditions of his experiment. The yield of β-methylglucoside is equal to about 20 per cent. of the glucose taken.

Ter Meulin[2] points out that in determining the nature of a sugar contained in a glucoside, hydrolysis should be effected by means of an enzyme and not by a dilute acid, since his experiments go to show that in the latter case the process is carried further. The same author has also made experiments illustrating the fact that the enzyme hydrolysis of glucosides can be retarded by addition of one of the reaction products; by enzyme hydrolysis of glucosides in contact with different sugars, under the same conditions, he was able to show that less decomposition occurs in cases where the added sugar is identical with that resulting from the hydrolysis of the glucoside.

It has been shown by Purdie and Irvine[3] that when a solution of tetramethylglucose in pure benzene containing hydrogen chloride is heated at 105—115° water is eliminated and the rotatory power increased. The product, when distilled under reduced pressure, was a neutral dextrorotatory syrup without multirotation, which did not reduce hot Fehling's solution. Analysis and determination of the methoxy-groups indicate that this product is an octamethylated disaccharide. Hydrolysis with dilute hydrochloric acid gave tetramethylglucose apparently as the sole product. It would appear that condensation had occurred between two molecules of tetramethylglucose in the γ-oxidic form, the product being an octamethylglucosidoglucoside. Apparently this is the first example of a synthesised disaccharide of the non-reducing type, of which cane sugar and trehalose are representative.

Irvine and Moody[4] in the course of an investigation on alkylated sugars have prepared and described tetramethylmannose and the isomeric tetramethyl α- and β-methylmannosides. The results are on the whole strictly comparable with those obtained in the study of the corresponding glucose and galactose compounds.

It has been shown by Cross, Bevan, and Briggs[5] that by treating cellulose with mixtures of acetic anhydride and acetic acid in presence of increasing quantities of sulphuric acid a series of acetosulphuric

[1] *Bull. Soc. chim.*, 1905, [iii], **33**, 469.
[2] *Rec. Trav. chim.*, 1905, **24**, 444.
[3] *Trans.*, 1905, **87**, 1022.
[4] *Ibid.*, 1462.
[5] *Ber.*, 1905, **38**, 1859.

esters is produced. Their formation takes place in a graduated way, and the particular equilibrium attained is dependent on the concentration of the sulphuric acid present in the mixture. By treatment with solvents such as acetone, alcohol, and water, these products can be approximately separated. One of these esters, which the authors term the normal acetosulphate, has the composition

$$(C_6H_7O_2)_4SO_4(C_2H_3O_2)_{10};$$

it is insoluble in water, but has the property of absorbing water to a remarkable extent, forming a hydrated jelly. It is soluble in acetone and in hot alcohol. Saponification with alcoholic potash fails to split off the SO_4 group, the resulting product being a water-soluble cellulose sulphate. The fact that this compound contains four C_6 residues to one SO_4 group would appear to afford additional proof that cellulose behaves in its reactions as a complex containing at least 24 carbon atoms.

Owing to the colloidal and hygroscopic character of these esters, their analysis was in the first instance a matter of some difficulty. In a later communication, however,[1] the authors show that by pouring the reaction mixture into amyl alcohol and washing the resulting precipitate with the same solvent the product may be dried at 100° without decomposition. Under these conditions, the compound behaves as a neutral sulphate, but in contact with water the SO_4 residue assumes the acid form, reacting with bases as the group SO_4H. The calcium, magnesium, and zinc salts have been prepared and analysed.

The authors are of opinion that these results confirm the conclusions at which they previously arrived[2] with regard to the simultaneous reaction of nitric and sulphuric acids with the hydroxyl groups in cellulose in the ordinary process of preparing cellulose nitrates; they explain also the mechanism of the ordinary practical methods for rendering these esters stable. From the general character of these ester reactions, the authors consider "that the reacting unit of cellulose is not of fixed dimensions, but combines in continuous and progressive proportions with negative groups to form these synthetical derivatives. In other words, as in the reactions of solutions it is generally held that it is not the molecules which react but the ionised fractions of these, so in cellulose the complex reacts as a *solution*, and while the stoichiometrical proportions of the interacting groups are, of course, experimentally verifiable, the molecular interpretation of the reactions is certainly not reconcilable with the experimental facts. Positive evidence is available that the colloidal characteristics of these compounds, which are maintained undisturbed by the reactions, are an essential condition of chemical constitution and function, and not merely an incidental 'physical' property."[3]

[1] *Ber.*, 1905, **38**, 3531. [2] *Ibid.*, 1901, **34**, 2496. [3] *Chem. Zeit.*, 1905, **29**, 527.

Le Sueur has shown [1] that when α-hydroxystearic acid is heated to 270° it decomposes into carbon monoxide, water, formic acid, margaric aldehyde, and the lactide of α-hydroxystearic acid. A similar decomposition is now found by the author [2] to occur in the cases of the α-hydroxy-derivatives of margaric, palmitic, pentadecylic, and myristic acids. The yield of the aldehyde in these cases is never less than 35 per cent. of the theoretical; the products are white solids and form oximes, semicarbazones, hydroxycyanides, &c., characteristic of aldehydes. They polymerise on keeping, the resulting compounds being trimolecular. These polymerides do not form oximes, semicarbazones, &c., and do not reduce potassium permanganate; when slowly distilled under reduced pressure, they are reconverted into the original aldehydes. The above-mentioned action affords, as previously pointed out, a convenient method, not only of preparing aldehydes of this class, but also of systematically degrading the aliphatic acids.

Garzarolli-Thurnlackh in 1892, by heating chloral and malonic acid in molecular proportions with excess of acetic acid, obtained γ-trichloro-β-hydroxybutyric acid, $CCl_3 \cdot CH(OH) \cdot CH_2 \cdot CO_2H$, and this when acted on by a concentrated solution of potassium or barium hydroxide gave rise to malic acid. Doebner and Segelitz [3] find that the yield is improved if pyridine is used in place of acetic acid, and they have extended the method to the preparation of substituted malic acids. By the condensation of chloral with ethylmalonic acid in presence of excess of pyridine, α-ethyl-β-hydroxy-γ-trichlorobutyric acid is obtained, and this, when warmed with aqueous (10 per cent.) caustic potash for an hour, acidified, evaporated, and extracted with ether, gave a theoretical yield of *β-ethylmalic acid*,

$$CCl_3 \cdot CH(OH) \cdot CHEt \cdot CO_2H + 5KOH = CO_2H \cdot CH(OH) \cdot CHEt \cdot CO_2H + 3KCl + 3H_2O.$$

The product is less hygroscopic than malic acid and melts at 86°; when heated at 200°, it gives rise to ethylmaleic acid. It is not identical with the ethylmalic acid which Fichter and Goldhaber obtained (1904) by reduction of ethyl oxalacetate with aluminium amalgam; their product melted at 133° and on heating gave methylcitraconic acid as the principal product.

β-Benzylmalic acid was similarly prepared from benzylmalonic acid, chloral, and pyridine. It melts at 155° and when heated to 200° gives phenylitaconic acid; it is presumed that phenylcitraconic (benzylmaleic) acid is first formed and undergoes transformation into the isomeride.

Only one modification of glutaconic acid has, up to the present

[1] Compare *Ann. Reports*, 1904, 62. [2] *Trans.*, 1905, **87**, 1888.
[3] *Ber.*, 1905, **38**, 2733.

time, been isolated, although from the generally accepted formula, $CO_2H{\cdot}CH_2{\cdot}CH{:}CH{\cdot}CO_2H$, the *cis*- and *trans*-modifications are to be expected. Such forms have, in fact, been shown to exist in *aa*-dimethylglutaconic acid and in aaa_1-trimethylglutaconic acid.[1] A series of experiments has now been carried out by Perkin and Tattersall with the object of preparing a second modification of glutaconic acid itself,[2] and although in this they were unsuccessful their results throw an important new light on the problem. They show in the first instance that glutaconic anhydride may be distilled without decomposition and they confirm Buchner's observation that on hydrolysis it yields the same modification of the acid from which it was prepared and which is therefore the *cis*-form. It is shown, further, that removal of the elements of hydrogen chloride from the ethyl ester of β-chloroglutarate, $CO_2Et{\cdot}CH_2{\cdot}CHCl{\cdot}CH_2{\cdot}CO_2Et$, and subsequent hydrolysis gives again only the *cis*-acid, although a similar procedure in the case of a substituted aaa_1-trimethylglutaconic acid yields the *trans*-form. From these and other observations, the authors consider that the generally accepted formula for glutaconic acid does not always correctly represent its constitution and that many of the remarkable properties of the acid would be more satisfactorily indicated by the symmetrical expression

$$CO_2H{\cdot}\underset{|}{CH}{\cdot}CH_2{\cdot}\underset{|}{CH}{\cdot}CO_2H.$$

This might be regarded as a tautomeric modification of the usual formula, one type being converted into the other during the course of certain reactions.

Thorpe, who has made a complete study of the methyl derivatives of glutaconic acid,[3] comes to a similar conclusion. He shows that the $a\beta$-derivatives are identical with the $\beta\gamma$-derivatives, that is, that the positions a and a_1 are identical and suggests for glutaconic acid the formula $CO_2H{\cdot}CH\begin{array}{c}CH\\ \vdots\\ H\end{array}CH{\cdot}CO_2H$, in which the dotted lines represent a state of equilibrium between the hydrogen and the two a-carbon atoms.

Reference was made in last year's Annual Report (p. 72) to the comparatively limited state of our knowledge of the dihydroxy-derivatives of acids of the succinic series other than the tartaric acids, and attention was drawn to the work of Rosenlew on isomeric dihydroxy-adipic acids. Kiliani and Herold [4] and Kiliani and Loeffler [5] have

[1] Perkin and Smith, *Trans.*, 1903, **83**, 8, 771; 1904, **85**, 155.
[2] *Trans.*, 1905, **87**, 361.
[3] *Ibid.*, 1669.
[4] *Ber.*, 1905, **38**, 2671.
[5] *Ibid.*, 3624.

recently published further investigations on the dihydroxyglutaric acids. It was shown by Kiliani in 1885 that *iso*saccharin (prepared by action of calcium hydroxide on milk sugar), when oxidised by nitric acid, yields glycollic acid and an unstable tribasic acid, $C_3H_3(OH)_2(CO_2H)_3$ (dihydroxypropenyltricarboxylic acid), and that the latter on being heated loses carbon dioxide, yielding a dihydroxyglutaric acid. This product differed in properties from the $\alpha\beta$-dihydroxyglutaric acid prepared from glutaconic acid dibromide, and was therefore represented as the $\alpha\gamma$-compound,

$$CO_2H\cdot CH(OH)\cdot CH_2\cdot CH(OH)\cdot CO_2H.$$

This constitution is supported in an indirect way by the observation of Ruff, Meusser, and Franz[1] that *iso*saccharin, when oxidised with hydrogen peroxide in presence of iron, gives rise to a keto-pentose, $C_5H_{10}O_4$; in this case, *iso*saccharin must have a hydroxyl group in the α-position. For the preparation of the above-mentioned tricarboxylic acid, the authors now recommend the oxidation of calcium *iso*saccharinate with strong nitric acid; by removal of resulting oxalic acid and concentration in a vacuum, the product is obtained in deliquescent plates or prisms. The constitution of the tricarboxylic acid is evidently represented by the formula

$$CO_2H\cdot C(OH)(CO_2H)\cdot CH_2\cdot CH(OH)\cdot CO_2H.$$

By boiling the acid calcium salt of this acid with the calculated quantity of oxalic acid and evaporating the resulting solution, the lactone of $\alpha\gamma$-dihydroxyglutaric acid is obtained, and from the calcium salt of this lactone the free acid is prepared in a similar way on allowing the solution to concentrate in a vacuum desiccator. This $\alpha\gamma$-acid melts at about 120° and yields a quinine salt containing $4H_2O$. It is further shown that the $\alpha\beta$-acid can be obtained from glutaconic acid not only by the bromine method above referred to, but also by oxidation with potassium permanganate; it melts and decomposes at 164°, and is optically inactive.

By oxidation of metasaccharopentose with dilute nitric acid at 35°, another $\alpha\beta$-dihydroxyglutaric acid is obtained, which is dextrorotatory and melts at 156°.

By hydrolysis of the glucoside "β-digitoxin," Kiliani in 1895 obtained a crystalline substance named by him *digitoxose*, which at first sight appeared to resemble glucose; analysis, however, showed that it has the composition $C_6H_{12}O_4$. It gives a blue colour with ferric chloride and yields an oxime, but no osazone. The constitution of this substance was for a considerable time a matter of doubt, but the same author shows now[2] conclusively that it is an aldose having the formula $CH_3[CH\cdot OH]_3\cdot CH_2\cdot CHO$. When oxidised by bromine, it yields the corresponding acid, $C_6H_{12}O_5$, and by oxidation with nitric

[1] *Ber.*, 1902, **35**, 2367. [2] *Ibid.*, 1905, **38**, 4040.

acid it gives rise to a dihydroxyglutaric acid, which appears to be one of the $\alpha\beta$-compounds.

A *trihydroxyadipic acid* melting at 146° was obtained by Kiliani in 1885 by oxidation of metasaccharin by nitric acid; the same author[1] has now prepared an acid which is probably a structure-isomeride of this by oxidation of the lactone of digitalonic acid. This new trihydroxyadipic acid melts at 124° and has the constitution $CO_2H[CH{\cdot}OH]_3{\cdot}CH_2{\cdot}CO_2H$, that from metasaccharin being

$$CO_2H[CH{\cdot}OH]_2{\cdot}CH_2{\cdot}CH(OH){\cdot}CO_2H.$$

Mesoxalic acid may conveniently be prepared by action of mercuric oxide on dihydroxytartaric acid in aqueous solution at 50°,[2] and ethyl mesoxalate by action of oxides of nitrogen on ethyl malonate at $-15°$.[3]

It is, of course, well known that ammonia, or primary or secondary amines, can react with formaldehyde even at the ordinary temperature, giving condensation products with elimination of water. When, however, these bases are heated with formaldehyde to about 120—160° in closed vessels, the course of the reaction is different, the result then being the replacement of amino- or imino-hydrogen by methyl. The principle of the latter change formed the subject of a patent by Eschweiler in 1893, but since it appears to have escaped the attention of chemists the author now gives a supplementary account of the process.[4] With ammonia, the resulting changes may be represented as follows:

$$2NH_3 + 3CH_2O = 2NH_2{\cdot}CH_3 + CO_2 + H_2O.$$
$$2NH_3 + 6CH_2O = 2NH(CH_3)_2 + 2CO_2 + 2H_2O.$$
$$2NH_3 + 9CH_2O = 2N(CH_3)_3 + 3CO_2 + 3H_2O.$$

Hexamethylenetetramine heated with excess of formaldehyde also yields trimethylamine, a circumstance which explains the odour of amines usually observed in the preparation of hexamethylenetetramine.

Primary and secondary amines behave in quite an analogous manner, dimethylethylamine being obtained from ethylamine, tetramethylethylenediamine from ethylenediamine, methylpiperidine from piperidine, and so on. This process forms a very convenient and simple method for the preparation of trimethylamine in quantity; by heating 50 grams of ammonium chloride with 40 per cent. formaldehyde solution in an autoclave to 120°, Koeppen[5] obtained a yield of 70—80 grams of trimethylamine hydrochloride.

[1] *Loc. cit.*, 3621.
[2] Fenton, *Trans.*, 1905, **87**, 813.
[3] Schmitt, *Compt. rend.*, 1905, **141**, [i], 48; and Curtis, *Amer. Chem. J.*, 1905, **33**, 603.
[4] *Ber.*, 1905, **38**, 880.
[5] *Ibid.*, 882.

Bearing in mind the interesting characters and properties of the tetralkylammonium hydroxides and the extent to which they have been employed in chemical and physical investigations, it is somewhat remarkable, as pointed out by Walker and Johnson,[1] that the free bases have never been isolated in any definite form. The solutions resulting from the interaction of alkyl iodides and silver oxide yield, it is true, a crystalline mass on evaporation, but the pure products have not been definitely isolated and analysed. By acting on tetramethylammonium chloride with potassium hydroxide in methyl-alcoholic solution, these authors obtained a product which by treatment with water and distillation yielded a crystalline pentahydrate of tetramethylammonium hydroxide. Concentration of the mother liquor from these crystals gave a trihydrate, and by dehydration of the pentahydrate at 35°/18 mm. a monohydrate was obtained. Under no conditions, however, was it found possible to obtain the anhydrous base, since the monohydrate decomposes with formation of trimethylamine before a temperature is reached at which its water-vapour pressure is appreciable.

In accordance with the observations of Külz (1871) and Baumann (1882), cysteine and cystine were formerly represented by the constitutional formulæ

$$CH_3{\cdot}C(NH_2)(SH){\cdot}CO_2H \text{ and } [CH_3{\cdot}C(NH_2)(CO_2H){\cdot}S{-}]_2.$$

But the investigations of Friedmann and of Neuberg in 1902 established the fact that the nitrogen and sulphur in these compounds are associated with different carbon atoms. From Friedmann's results and from the recent synthesis by E. Erlenmeyer, jun.,[2] there is now little if any doubt that the two compounds are correctly represented by the constitution

$$CH_2(SH){\cdot}CH(NH_2){\cdot}CO_2H \text{ and } [{-}S{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CO_2H]_2.$$

Before the conclusion of these last-named investigations there remained yet the alternative formulæ

$$CH_2(NH_2){\cdot}CH(SH){\cdot}CO_2H \text{ and } [{-}S{\cdot}CH(CO_2H){\cdot}CH_2{\cdot}NH_2]_2,$$

and researches were carried out by Gabriel with the object of synthetically producing compounds of these constitutions. The author has now succeeded in effecting this synthesis, and the compounds obtained are named by him iso*cysteine* and iso*cystine*.[3] The method employed was briefly as follows: dihydrouracil (or β-lactylurea), $CH_2\begin{matrix}CH_2{\cdot}NH\\CO{-}NH\end{matrix}>CO$, was converted into the bromo-derivative

[1] *Trans.*, 1905, **87**, 953. [2] See *Ann. Reports*, 1904, 75.
[3] *Ber.*, 1905, **38**, 630.

and, by action of potassium thiocyanate, the bromine atom was replaced by the CNS group. This thiocyanyl derivative when heated to 170° in a sealed tube with fuming hydrochloric acid is converted into the hydrochloride of *iso*cysteine. Iodine converts the latter into the hydriodide of *iso*cystine:

$$2C_3H_7O_2NS + I_2 = C_6H_{12}O_4N_2S_2 + 2HI.$$

The free base melts at 185°; it differs from cystine in giving a dark brown coloration when warmed with copper sulphate in hydrochloric acid solution and a black colour with alkaline lead solutions even in the cold.

According to the investigations of Neuberg, Loewy, and Mayer, it appears that calculus-cystine differs both physiologically and chemically from protein-cystine, which is derived from hair, horn, &c. It might at first sight seem probable that this difference is to be explained by the two alternative formulæ above mentioned, but although it is fairly certain that protein-cystine is correctly represented by Friedmann's α-amino-β-thio-constitution, the properties of calculus-cystine differ somewhat from those of Gabriel's synthetical product. Since the latter is the α-thio-β-amino-compound, the constitution of calculus-cystine cannot be regarded as finally settled.[1] Experiments of Fischer and Suzuki[2] suggest the possibility that the differences observed in calculus cystine may be due to the presence of tyrosine as an impurity. By suspending cystine in absolute methyl alcohol and passing hydrogen chloride into the mixture they obtain the hydrochloride of cystine dimethyl ester, $C_8H_{16}O_4N_2S_2$; this and the corresponding nitrate, sulphate, and picrate are crystalline salts which serve for the identification of cystine. Treated in this way, both calculus-cystine and protein-cystine gave identical products.

The behaviour of urea when treated with hypobromites and hypochlorites has been the subject of quite an extraordinary number of independent researches during the last fifty years, and it would naturally be supposed that the nature of the change, apparently so simple, must have been exhaustively established. It comes as a surprise, therefore, to learn from Schestakoff[3] that by the action of sodium hypochlorite and sodium hydroxide at about 5° urea can be made to yield hydrazine. This result, which was predicted by the author from analogy with Hofmann's well-known conversion of amides to amines, would appear to be reached in the following stages:

[1] Compare Neuberg and Mayer, *Zeit. physiol. Chem.*, 1905, **44**, 472.
[2] *Zeit. physiol. Chem.*, 1905, **45**, 405.
[3] *J. Russ. Phys. Chem. Soc.*, 1905, **37**, 1.

(1) $NH_2 \cdot CO \cdot NH_2 + NaClO = NH_2 \cdot C(ONa) : NCl + H_2O$.
(2) $NH_2C(ONa) : NCl = NH_2 \cdot N : C(ONa) \cdot Cl$.
(3) $NH_2 \cdot N : C(ONa) \cdot Cl + NaOH = NH_2 \cdot NH \cdot CO_2Na + NaCl$.
(4) $NH_2 \cdot NH \cdot CO_2Na + H_2O = NH_2 \cdot NH_2 + NaHCO_3$.

Hydrazine is of course immediately oxidised by hypochlorites with evolution of nitrogen, but by having present a substance which reacts with hydrazine to form a difficultly oxidisable product this decomposition is avoided. For this purpose, a suitable agent was found in benzaldehyde, which reacts with the hydrazine at the moment of its formation to give benzalazine, $C_6H_5CH : N \cdot N : CHC_6H_5$. By addition of sulphuric acid and removal of the benzaldehyde in steam, the hydrazine is obtained in the form of sulphate. The yield is said to be 60 per cent. of that required by theory, and from one litre of urine the author obtained 30—40 grams of hydrazine sulphate. Substituted ureas similarly yield corresponding hydrazines, benzoylurea, for example, giving benzoylhydrazine.[1] It is somewhat difficult at first sight to reconcile the facts here recorded with some of the conclusions which have been drawn by previous observers. It was shown, for example, by the present writer in 1878 that when urea is acted on by hypochlorites in presence of caustic alkali, one-half of the nitrogen is evolved in the free state, the other half remaining as cyanate. This result was easily explained in view of the further observation (1888) that the transformation of ammonium cyanate into urea is a limited and reversible reaction, a result which was afterwards confirmed in a different manner by Walker and Hambly (1895). The conditions under which Schestakoff's experiments were carried out, however, differed very considerably from those of previous observers in that he used only the calculated quantities of hypochlorite and soda and operated at a low temperature.

The explanation previously suggested [2] of the hypochlorite action was that urea itself is not acted on by the agent, and that the nitrogen comes only from the ammonium group after reversion of the urea has taken place. Possibly both actions, the oxidation of urea itself and the reversion, take place simultaneously, but at the lower temperature the latter change is too slow to be very appreciable, and the principal result is then the oxidation of urea to hydrazine.[3]

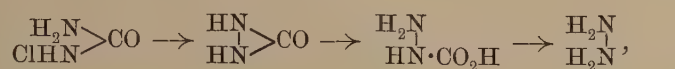
Armstrong and Robertson [4] point out that Schestakoff's result has an important bearing on the theory that nitrogen in conjunction with

[1] *Chem. Centr.*, 1905, ii, 1703. [2] Fenton, *Proc.*, 1895, **11**, 138.

[3] It may be mentioned that E. P. Frankland, who is now working in the Cambridge University Laboratory, has carefully repeated Schestakoff's experiments, and is able entirely to confirm the latter's statements, except that the yield of hydrazine obtained was very much smaller than that above mentioned.

[4] *Trans.*, 1905, **87**, 1286.

carbon has a tendency to give rise to three atom rings as a preferred form; they suggest that the reaction in question may be represented as taking place in the following stages:



Hofmann's conversion of acetamide into methylamine being formulated as:

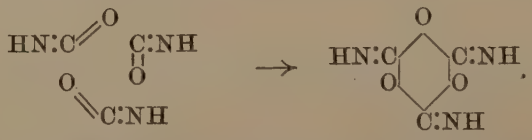
The interaction of dry carbon monoxide and ammonia when the gases are heated in presence of platinum has hitherto been represented by the relation $CO + 2NH_3 = NH_4 \cdot CN + H_2O$,[1] but it is now shown by Jackson and Northall-Laurie that the main product is ammonium cyanate, which, as the temperature rises, is converted into urea. The change may be brought about not only by passing the gases over a heated platinum spiral or platinised asbestos, but also by ordinary sparking. Similar results are obtained by using the silent discharge, but in this case polymerised cyanogen compounds are also produced. Water, methane, hydrogen, and nitrogen are found amongst the gaseous products, and the authors consider that the initial change may be $CO + 2NH_3 = NH_4 \cdot CNO + H_2$, and that methane results from the interaction of carbon monoxide with the free hydrogen.

By the action of ammonia on carbonyl chloride, dissolved in light petroleum at 0°, there is formed not only urea but also cyanuric acid and cyamelide.[2] Melanurenic acid (the monamide of cyanuric acid), as first pointed out by Bouchardat, is also produced when the substances react in the gaseous state.[3]

It is sometimes stated that cyamelide is produced, together with cyanuric acid, when urea is heated. This, according to Hantzsch,[4] is not the case; a substance is produced, however, which at first sight appears closely to resemble cyamelide, but differs from it in being soluble without decomposition in boiling water. This substance, which exhibits both basic and acidic properties, is proved to be the ureide of cyanuric acid or tricyanocarbamide, $(CN)_3(NH \cdot CO \cdot NH_2)_3$. It is also formed by heating urea with cyanogen bromide to 150°, or with cyanuric acid to 180°. The same compound is formed when biuret is heated, the change being probably in the first instance $NH_2 \cdot CO \cdot NH \cdot CO \cdot NH_2 = NH_2 \cdot CO \cdot NH \cdot CN + H_2O$, this resulting cyanurea then undergoing polymerisation.

[1] Kuhlmann, 1841.
[2] Hantzsch and Stuer, *Ber.*, 1905, **38**, 1042.
[3] Stuer, *ibid.*, 2326.
[4] *Ber.*, 1905, **38**, 1013.

No direct determination of the molecular weight of cyamelide has yet been made owing to its insolubility in ordinary solvents, but the author comes to the conclusion, by indirect evidence, that it has the same molecular weight as cyanuric acid, cyamelide and cyanuric acid being isomeric and not polymeric. The conversion of cyanic acid to cyamelide is known to be a trimolecular reaction; this fact and also the composition of the mercuric derivative of cyamelide which the author has obtained indicate $(HCNO)_3$ as the minimum formula, and many reasons are adduced for considering that this is likewise the maximum. Cyamelide is more easily decomposed (by sulphuric acid, for example) than cyanuric acid; the fact that in many reactions the opposite appears to be the case is explained by saying that cyanuric acid is a pseudo-acid which is easily convertible into the more reactive true acid. It is shown that cyamelide cannot be regarded as a tricyanogen derivative, neither can it contain the salt-forming group –N:C·OH or the "indirect" salt-forming group –NH·CO; these and other considerations lead to the conclusion that cyamelide is to be regarded as a polymeride of pseudo-cyanic acid, OC:NH, and not of cyanic acid, HO·CN, its formation being represented as:



Although the molecular formula for fulminic acid has been sometimes expressed as $(CHNO)_2$—this formula appearing on the whole to be the most consistent with the reactions of its derivatives—the question could not be regarded as settled, since there appeared to be certain facts (for example, the non-existence of acid salts and the synthesis of fulminates from mono-carbon compounds such as nitroethane) which were more in accord with the single formula. Wöhler and Theodorovits[1] have now made a study of the formation of mercury fulminate from a variety of carbon compounds by the usual method of treatment with strong nitric acid and mercuric nitrate. They come to the conclusion that mono-carbon compounds do not give fulminate by this treatment, and the same appears to be the case with compounds containing three or more carbon atoms, whereas many of the 2-carbon series yield the pure product, although in all cases a very considerable excess of the carbon compound has to be employed. Since, however, negative results were obtained with glycol, glyoxal, glyoxime, and acetonitrile, the authors conclude that a 2-carbon chain of a certain structure (for example, methyl groups in

[1] *Ber.*, 1905, **38**, 1345.

conjunction with $-CH_2\cdot OH$, $-CH<^{O-}_{O-}$, $-C\leqslant^{H}_{O}$, or $=CH\cdot O-$) is necessary for fulminate formation by this treatment. These results appeared therefore to favour the bimolecular formula for fulminic acid.

But Wöhler[1] has further made determinations of the molecular weight of sodium fulminate, which can be prepared in a pure anhydrous state by the action of sodium amalgam on mercury fulminate suspended in alcohol.

The numbers obtained by the cryoscopic method, assuming that sodium fulminate is ionised to the same extent as other salts of analogous constitution under similar conditions, correspond closely with the theoretical value required for the single formula NaCNO. Determination of the equivalent conductivities at 0° of the solution at dilutions of $N/32$ and $N/1024$ lead to a similar result, sodium fulminate behaving as the salt of a monobasic acid; in this case, the measurements could not be carried out at 25° as in Ostwald's experiments, since the solution shows signs of decomposition at this temperature.

By the action of nitric acid on ethyl acetonedicarboxylate, an oil is obtained which, according to Ulpiani and Bernardini, is the peroxide of ethyl oximinoacetate; the same compound results also from the action of fuming nitric acid on ethyl acetoacetate. When this compound is treated with concentrated ammonia it is converted quantitatively into a compound having the formula $(CHON)_x$. These authors now show[2] that the latter compound is succinamidedinitrosoperoxide. When this is boiled with concentrated ammonia, it gives rise to fulminuric acid and *iso*fulminuramide. The fulminuric acid so obtained is identical with that obtained by Liebig from mercuric fulminate by action of alkali chlorides and is considered by the authors to have the constitution $NO_2H{:}C(CN)\cdot CO\cdot NH_2$.

Researches on the synthesis of polypeptides continue to be actively carried on by Emil Fischer and his colleagues.[3] Results of considerable importance have been arrived at, and a large number of new polypeptides, of very varying types, has been synthesised. It would be quite impossible in the short space here available to give anything like a useful account of these later results, which in their present state refer principally to matters of detail and, in part, belong more appropriately to the domain of Physiological Chemistry. It is pointed out that a study of the polypeptides offers special advantages in dealing with certain problems in stereochemistry owing to the

[1] *Ber.*, 1905, **38**, 1351. [2] *Gazzetta*, 1905, [ii], **35**, 7.

[3] *Ber.*, 1905, **38**, 605, 2375, 2914; *Annalen*, 1905, **340**, 123, 128, 142, 152, 168, 172, 180, 190.

large number of asymmetric carbon atoms which can be introduced into some of the higher members. Optically active polypeptides have hitherto been prepared only from active amino-acids, but it has now been found possible to build up members of this class by using optically active or racemic acid chlorides.

An improved method of obtaining amino-acid chlorides, which is applicable to those of a complex character, has been devised. This consists in heating the acids with a mixture of acetyl chloride and phosphorus pentachloride.

The polypeptides when melted yield anhydrides or diketopiperazines, and these by the action of dilute alkalis yield the salt of a higher member; thus glycine anhydride gives the sodium salt of glycylglycine when shaken with normal solution of caustic soda; alanylalanine can similarly be obtained from alanine-anhydride.

It will be noticed from the structural formulæ that each diketopiperazine with a side-chain corresponds to two different polypeptides, thus leucylglycine, $(CH_3)_2{\cdot}CH{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CO_2H$, and glycyl-leucine, $NH_2{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}CH(C_4H_9){\cdot}CO_2H$, each give on melting the same anhydride, *iso*butyldiketopiperazine,

$$(CH_3)_2CH{\cdot}CH_2{\cdot}CH{\cdot}NH{\cdot}CO$$
$$\qquad\qquad\qquad\quad CO{-}NH{\cdot}CH_2$$

H. J. H. Fenton.

ORGANIC CHEMISTRY—HOMOCYCLIC DIVISION.

During the past year, the contributions to the chemistry of the homocyclic division of the aromatic compounds have not been marked by any discoveries of exceptional interest. The advances have followed the lines of former work, and very little new ground has been broken.

The study of the relation of colour to structure, which engaged so much attention in the past year, has made little real progress. The writer ventures to offer the opinion that, in the present state of our knowledge, any explanation of colour which finds its final expression in terms of structural formulæ, based on chemical changes alone, will be as inconclusive as the derivation of structural formulæ from the mere attribute of colour. It is for this reason that the valuable data on absorption spectra, which are being accumulated by Hartley, Dobbie, Baly, and other workers in this field, will be followed with special interest.[1]

The growing importance of the industry which is best described by the German "Riechstoffe," and the theoretical value of a correct knowledge of these widely distributed products of vegetable life, is reflected in the increasing attention which is being given to the study of hydrocyclic compounds.

Reagents.

Phenylcarbimide, which has been regarded as a trustworthy reagent for hydroxy-compounds in non-dissociating solvents, has been shown by Dieckmann, Hoppe, and Stein[2] to have forfeited to some extent its character. They find that among 1 : 3-diketones this reagent in presence of a trace of alkali may form *C*-carbanilido-compounds,

$$\begin{matrix}\mathrm{R{\cdot}CO}\\ \mathrm{R{\cdot}CO}\end{matrix}\!\!>\!\mathrm{CH_2} + \mathrm{C_6H_5{\cdot}NCO} = \begin{matrix}\mathrm{R{\cdot}CO}\\ \mathrm{R{\cdot}CO}\end{matrix}\!\!>\!\mathrm{CH{\cdot}CO{\cdot}NH{\cdot}C_6H_5},$$

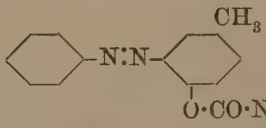
but the reaction is inhibited if the carbimide is pure. On the other hand, hydroxymethylene compounds and cyclic hydroxy-compounds (hydroresorcinols and phenols) combine to form *O*-carbanilido-deriv-

[1] Since this paragraph was written, an interesting paper by Professor Hartley has appeared on the subject of colour in its relation to structure, which is based on observations of absorption spectra of colourless and coloured substances (*Trans.*, 1905, **87**, 1822).

[2] *Ber.*, 1904, **37**, 4627.

atives, but whereas the cyclic compounds combine in absence of alkali, the hydroxymethylene compounds do not. They conclude that the use of phenylcarbimide as a reagent for determining constitution of tautomeric 1 : 3-diketones is subject to obvious limitations. Goldschmidt and Löw-Beer[1] have also found that the distinction which they formerly drew between *o*- and *p*-hydroxyazo-compounds on the strength of the phenylcarbimide reaction must be revised. The para-compounds, which readily combine with this reagent, were regarded as true phenols, whereas the ortho-compounds, which did not, were represented as quinone derivatives.

Both series of compounds have now been proved to form carbanilido-compounds, and therefore possess the same structure. It appears, further, that in the special case investigated, that of benzeneazo-*p*-cresol, the phenylcarbimide molecule attaches itself to the hydroxyl group :



The authors conclude from this and other reasons which cannot be fairly condensed into a small compass that the hydrazine formula for hydroxyazo-compounds is no longer tenable, and the same applies to aminoazo-compounds. Finally, Dimroth[2] has demonstrated the unreliability of phenylcarbimide for ascertaining the structure of diazoamino-compounds, which Busch and Bergmann[3] for other reasons also conclude must possess the normal constitution.

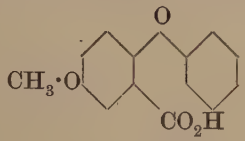
The use of copper as a catalytic agent, referred to in last year's report (p. 87), has been extended by Ullmann and his collaborators,[4] who now show that chlorine in *o*-chlorobenzoic acid and its derivatives may, in presence of small quantities of finely-divided copper, be replaced by phenol, thiophenol, arylamine, and arylsulphinic groups. To give a few examples, potassium *o*-chlorobenzoate, heated to 180—190° with sodium phenoxide in alcoholic solution to which a little copper powder is added, gives a 90 per cent. yield of *o*-phenoxybenzoic acid :

$$ClC_6H_4\cdot CO_2Na + NaO\cdot C_6H_5 = C_6H_5\cdot O\cdot C_6H_4\cdot CO_2Na + NaCl.$$

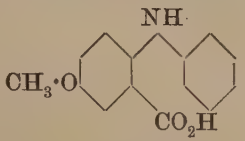
The latter can be readily converted into xanthone :

[1] *Ber.*, 1905, **38**, 1098.
[2] *Ibid.*, 675.
[3] *Zeit. Text. Farb. Ind.*, 1905, **4**, 105.
[4] *Ber.*, 1905, **38**, 729, 2120, 2211.

In the same way, 2-chloro-5-methoxybenzoic acid with phenol in the one case and aniline in the other yields 2-phenoxy-5-methoxybenzoic acid (I) and 4-methoxydiphenylamine-2-carboxylic acid (II), which can be converted respectively into xanthone and acridone derivatives :



I.



II.

By the use of metallic copper, phenoxides and bromobenzene or its derivatives give excellent yields of phenylated phenols.

Hinsberg's method [1] for separating primary and secondary amines by the aid of benzenesulphonic chloride, which was subsequently shown to be untrustworthy, has been modified by the substitution of β-anthraquinonesulphonic chloride for the former reagent in such a way as to render it applicable to the quantitative separation of the bases, but the details of the process are too intricate to be reproduced in a general report.[2]

A very interesting method has been devised by Wislicenus and Wren [3] for preparing both arylnitromethanes and stilbene derivatives concurrently. It may be illustrated in the case of benzyl cyanide, which was previously found to combine with ethyl nitrate in presence of sodium ethoxide [4] to form the sodium compound of phenyl*iso*nitroacetonitrile :

$$C_6H_5\cdot CH_2\cdot CN + C_2H_5\cdot O\cdot NO_2 = C_6H_5\cdot C(CN){:}NO\cdot ONa + C_2H_5\cdot OH.$$

When boiled with caustic soda, the latter loses cyanogen in the form of sodium carbonate and ammonia, and phenyl*iso*nitromethane results, which, however, rapidly isomerises to phenylnitromethane. At a higher temperature, it decomposes and yields stilbene :

$$2C_6H_5\cdot CH{:}NO\cdot ONa = C_6H_5\cdot CH{:}CH\cdot C_6H_5 + 2NaNO_2.$$

Formaldehyde has been employed in the synthesis of methylnaphthol by preparing in the first instance dihydroxydinaphthylmethane by condensing formaldehyde and naphthol and then reducing the product with zinc dust and alkalis,

$$CH_2(C_{10}H_6\cdot OH)_2 = CH_3\cdot C_{10}H_6\cdot OH + C_{10}H_7\cdot OH.^{5}$$

The use of sodamide as a condensing reagent is described on p. 108.

Patents have been taken out during the year for two new reagents ;

[1] *Ber.*, 1890, **23**, 2963. [2] *Ibid.*, 1905, **38**, 906. [3] *Ibid.*, 670.
[4] *Ibid.*, 1902, **35**, 1755. [5] *Zeit. Farb. Text. Ind.*, 1905, **4**, 265.

the Badische Anilin- & Soda-Fabrik [1] prepare manganese disulphate, $Mn(SO_4)_2$, by the action of electrolytic oxygen on manganous sulphate in presence of moderately strong sulphuric acid. In acid solution, the reagent possesses the power of oxidising the side-chain of aromatic hydrocarbons to aldehyde or acid as required. The other reagent is silicon fluoride, which Sommer [2] uses for the preparation of anhydrides by passing the gas into the heated salt of the acid.

Grignard's Reaction.—To judge from the uninterrupted stream of memoirs on the subject, the applications of Grignard's remarkable reaction are not yet exhausted. From the long list before us, those only have been selected which offer points of novelty.

Dimroth [3] finds that organo-magnesium compounds act on alkyl and aryl derivatives of azoimide (azides) in the following way :

$$RN<\begin{matrix}N\\ \|\\ N\end{matrix} + R^1MgX = RNMgXN{:}NR^1;$$

$$RNMgXN{:}NR^1 + H_2O = RNH{\cdot}N{:}N{\cdot}R^1 + MgX(OH),$$

and thus offer a means of preparing simple and mixed aliphatic diazo-amino-compounds which are not obtainable by Griess's reaction. Tschitschibabin [4] has introduced methods for obtaining acid esters and ortho-esters by the aid of ethyl carbonate and orthocarbonate. The first reaction passes through the following three phases :

1. $CO(O{\cdot}C_2H_5)_2 + RMgX = R{\cdot}C(O{\cdot}C_2H_5)_2OMgX.$
2. $R{\cdot}C(O{\cdot}C_2H_5)_2OMgX + RMgX = R_2C(O{\cdot}C_2H_5)OMgX + C_2H_5{\cdot}OMgX.$
3. $R_2C(O{\cdot}C_2H_5)OMgX + RMgX = R_3CO{\cdot}MgX + C_2H_5{\cdot}O{\cdot}MgX.$

On decomposing the product at each stage with water, the first yields an acid ester, the second a ketone, and the third a tertiary alcohol. With care, the operation may be arrested at the first stage and gives a yield of upwards of 80 per cent. of the theoretical amount of acid ester. In preparing the ortho-esters from ethyl orthocarbonate, the reaction proceeds as follows :

1. $C(O{\cdot}C_2H_5)_4 + RMgX = R{\cdot}C(O{\cdot}C_2H_5)_3 + C_2H_5{\cdot}OMgX.$
2. $R{\cdot}C(O{\cdot}C_2H_5)_3 + RMgX = R_2C(O{\cdot}C_2H_5)_2 + C_2H_5{\cdot}OMgX.$

The use of magnesium has been ingeniously applied to the preparation of sulphonic acids of the cyclo-paraffins, which, until now, have not been obtained. Borsche and Lange [5] have shown that cyclo-paraffinsulphinic acids, which are first formed by passing sulphur dioxide into the magnesium halogen compound of the paraffin, can be oxidised to the sulphonic acid. Hexahydrobenzenesulphonic acid has been prepared in this way :

$$C_6H_{11}MgCl \longrightarrow [C_6H_{11}SO_2]_2Mg \longrightarrow [C_6H_{11}SO_3]_2Mg.$$

[1] *Zeit. Farb. Text. Ind.*, 1905, **4**, 283. [2] *Ibid.*, 527.
[3] *Ber.*, 1905, **38**, 670. [4] *Ibid.*, 561. [5] *Ibid.*, 2766.

Grignard[1] has contributed a method for synthesising mono- and poly-hydric alcohols. The starting point is the chlorohydrin, which then passes through the following phases :

$$RMgX + CH_2Cl\cdot CH_2\cdot OH = RH + CH_2Cl\cdot CH_2\cdot OMgX.$$
$$R^1MgX = CH_2Cl\cdot CH_2\cdot OMgX = R^1CH_2\cdot CH_2\cdot OMgX + MgXCl.$$

The product, when decomposed with water, gives the monohydric alcohol $RCH_2\cdot CH_2\cdot OH$. With glycerol monochlorohydrin, a series of glycols has been obtained. The preparation of mixed thio-ethers has been effected by Taboury[2] by the action of alkyl halides on compounds of the formula RSMgBr, which in turn are prepared by the action of sulphur on the organo-magnesium compound. He has obtained in this way a variety of phenyl alkyl sulphides.

Bouveault[3] has devised a process for preparing aldehydes from substituted formamides which forms the subject of a patent. It may be formulated in the following way :

$$HCO\cdot NRR^1 + R^2MgX = HCR^2(OMgX)NRR^1.$$
$$HCR^2(OMgX)NRR^1 + H_2O = R^2CHO + NHRR^1 + Mg(OH)X.$$

The magnesium organic compound is prepared in the usual way, and to the boiling ethereal solution the disubstituted formamide dissolved in ether is gradually added. The product is decomposed with sulphuric acid and the ethereal solution removed and distilled.

The practical difficulty of inducing magnesium to combine with iodo-aniline and its derivatives has been overcome by Baeyer[4] by previously adding a little iodine to the metal and heating so as to form magnesium iodide. It has thus become possible to obtain a variety of amino-derivatives of triphenylcarbinol by uniting the magnesium compound of the base with benzophenone and its derivatives :

$$C_6H_5\cdot CO\cdot C_6H_5 + IMg\cdot C_6H_4\cdot N(CH_3)_2 = C_6H_5\cdot C\begin{matrix}<\\ \\ \\ \end{matrix}\begin{matrix}C_6H_5\\ C_6H_4\cdot N(CH_3)_2\\ OMgI\end{matrix}.$$

A further account of Grignard's reaction will be found on p. 114.

Reduction.—The reduction of benzonitrile with hydrogen in presence of copper or nickel, whereby Sabatier and Senderens obtained toluene and ammonia, has been shown by Frebault[5] to yield under modified conditions benzylamine and dibenzylamine, whilst toluonitrile gives rise to the corresponding homologous bases. It may be added that a very complete review of the various applications of this important

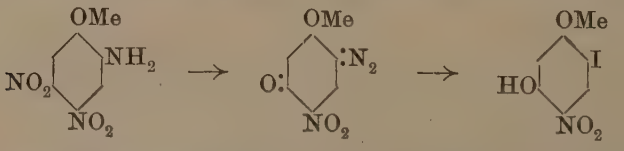
[1] *Compt. rend.*, 1905, **141**, 44.
[2] *Bull. Soc. chim.*, 1904, [iii], **31**, 1183.
[3] *Ibid.*, 1322.
[4] *Ber.*, 1905, **38**, 2759.
[5] *Compt. rend.*, 1904, **140**, 1036.

reduction method is given by its discoverers in the *Annales de Chimie et Physique* [1] for the present year. The electrolytic method for reducing acids which was initiated by Tafel and Friedrichs [2] has been further investigated by Mettler,[3] who finds that the aromatic acids are reduced to alcohols as readily as the esters; benzoic acid and its halogen and hydroxy-derivatives give the corresponding benzyl alcohols, and the nitrobenzoic acids, the aminobenzyl alcohols. In this process the nucleus is unaffected.

The preparation of arylhydroxylamines by the electrolytic reduction of nitro-compounds suspended in a solution of acetic acid and sodium acetate contained in a cathode cell is described by Brand.[4]

Diazotisation.—Those who have had occasion to submit a variety of amino-compounds to the action of nitrous acid will have experienced the unaccountable behaviour which they occasionally manifest. Diazonium salts are usually regarded as typically unstable substances, yet there are many examples which exhibit the contrary property. Meldola and Eynon [5] obtained an aminobenzenediazonium chromate which can be boiled in acetic acid and only explodes at 144—148°, and Cain [6] has prepared a coloured 3-ethoxydiphenyl-4-diazonium sulphate, $HO{\cdot}C_6H_4{\cdot}C_6H_3(O{\cdot}C_2H_5){\cdot}N_2{\cdot}HSO_4$, which withstands boiling with dilute sulphuric acid without change. A similar stable diazonium sulphate of 6-aminocoumarin,[7] as well as a stable diazonium carbonate and nitrite derived from *p*-aminobenzanilide,[8] are described by Morgan and Micklethwait, and in a patent specification of Bayer & Co.[9] it is stated that 1 : 4-diazohydroxyanthraquinone requires to be heated to 170—180° with strong sulphuric acid to convert it into quinizarin.

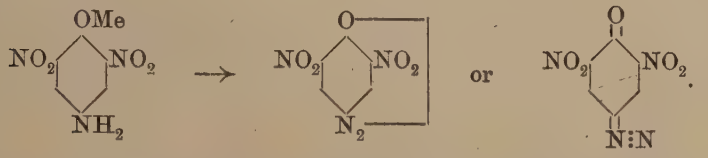
In 1901, Meldola and Eyre observed that when dinitroanisidine is diazotised it loses a nitro-group, the resulting compound being a diazide. By the action of iodine, the latter is converted into iodonitroresorcinol



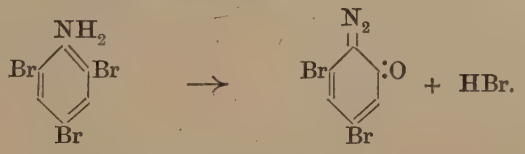
methyl ether,[10] the nitro-group in the para-position to the original amino-group being eliminated. If, however, the amino-group is in the para-position to the methoxy-group, no nitro-group is removed but methyl is displaced, and the resulting compound is a dinitroquinone-

[1] *Ann. Chim. Phys.*, 1905, [viii], **4**, 319, 433.
[2] *Ann. Reports*, 1904, 93.
[3] *Ber.*, 1905, **38**, 1745.
[4] *Ibid.*, 3076.
[5] *Trans.*, 1905, **87**, 2.
[6] *Ibid.*, 5.
[7] *Ibid.*, 1904, **85**, 1235.
[8] *Ibid.*, 1905, **87**, 933, 934.
[9] *Zeit. Farb. Text. Ind.*, 1905, **4**, 318.
[10] Meldola and Stephens, *Trans.*, 1905, **87**, 1199.

diazide. The compound investigated (2 : 6-dinitroaminoanisole) yields the following product :

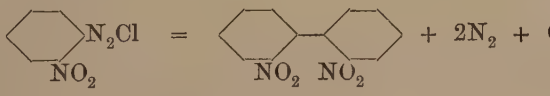


Similar observations have been made by Orton [1] in the case of the *s*-trihalogendiazonium salts of weak acids (the hydroxyl and diazonium ions may be supposed to be present in solution) when quinonediazide is formed with the elimination of bromine.



In presence of strong acids, the ordinary change to *s*-tribromophenol occurs. Orton, Coates, and Burdett [2] find, however, that the normal reaction may be produced in the first case by exposure to sunlight.

Ullmann and Frentzel [3] have made the curious observation that, by the action of cuprous chloride in hydrochloric acid on the diazonium salts of the isomeric nitranilines and their derivatives, the ordinary Sandmeyer reaction is subordinated to the production of diphenyl derivatives. *o*-Nitraniline, for example, gives an excellent yield of 2 : 2-dinitrodiphenyl :



Few examples of diazoalkylamino-compounds are known, for the product of the action of diazonium salts on primary alkylamines gives bisdiazoamino-compounds or compounds containing one molecule of amine united to two of the diazo-compound. Dimroth [4] has succeeded in obtaining true triazenes of the formula Ar·N:N·NH·Alk. In order to prepare phenylmethyltriazene, $C_6H_5 \cdot N{:}N \cdot NH,CH_3$, aniline is diazotised in the usual way, a little excess of nitrite is added, and the solution carefully neutralised with sodium carbonate. On the other hand, a methylamine solution is prepared also containing sodium carbonate, to which ice is added, and the liquid covered with a layer of ether. The diazo-solution is run in and the mixture stirred. The

[1] *Trans.*, 1903, **83**, 796.
[2] *Proc.*, 1905, **21**, 168.
[3] *Ber.*, 1905, **38**, 725.
[4] *Ibid.*, 2328.

triazene dissolves in the ethereal layer, which is separated at the end of the operation and the ether removed by distillation.

A series of diazoimides is described by Morgan and Micklethwait,[1] who obtained them by diazotising sulphonamides of *o*- and *p*-phenylenediamine in the usual way and precipitating the product with sodium acetate. The diazoimides of *d*-camphor-*β*-sulphonyl- and of benzenesulphonyl-*p*-phenylenediamine have the following formulæ:

$$C_6H_4\begin{cases}N\cdot SO_2\cdot C_{10}H_{15}O\\ N_2\end{cases} \qquad C_6H_4\begin{cases}N\cdot SO_2\cdot C_6H_5\\ N_2\end{cases}.$$

The difficulty experienced in obtaining hydrazines of the anthraquinone series has now been removed by Bayer & Co.[2] by reducing the diazosulphonate instead of the chloride or sulphate. The reaction proceeds quite smoothly and the products can be employed in the preparation of colouring matters.

Condensation.

Probably the most interesting development in this field of research is the introduction of sodamide by Claisen[3] as a new condensing agent. In the majority of cases, its action is quicker and more regular than either sodium or sodium ethoxide. It can be used in the synthesis of 1 : 3-diketones and for alkylating ketones. Acetophenone and ethyl iodide in presence of sodamide give ethylacetophenone. By the action of ethylchloroacetate on ketones, glycid-esters are formed. The latter reaction may be illustrated in the case of acetophenone, and probably proceeds in three phases. In the first, an additive compound with sodamide is formed, which undergoes condensation with the ethyl chloroacetate and is followed by the removal of sodium chloride.

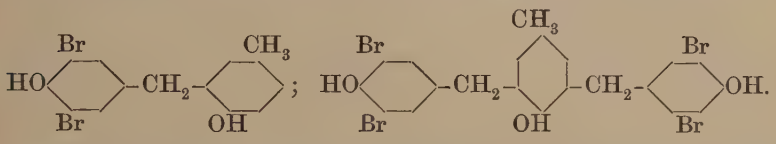
1. $C_6H_5\cdot C(CH_3)(ONa)\cdot NH_2$. 2. $C_6H_5\cdot C(CH_3)(ONa)CHCl\cdot CO_2\cdot C_2H_5$.
3. $C_6H_5\cdot C(CH_3)CH\cdot CO_2\cdot C_2H_5$.
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad \backslash O /$

In a paper which follows, Claisen reaffirms with little modification the position formerly held by him to explain the ethyl acetoacetate synthesis, which has been promptly criticised by his old opponent Michael.[4] Both papers, although too long to be summarised, are well worth perusal; they tend to show that the problem has not reached its final solution.

The study of condensation of pseudo-phenols with tertiary bases referred to in the previous Report (p. 101) has been extended by Auwers and Rietz[5] to phenols. Dibromo-*p*-hydroxybenzyl bromide,

[1] *Trans.*, 1905, **87**, 73, 922. [2] *Zeit. Farb. Text. Ind.*, 1905, **4**, 286.
[3] *Ber.*, 1905, **38**, 693. [4] *Ibid.*, 1922, 2523. [5] *Ibid.*, 3302.

for example, unites with phenols to form diphenylmethane derivatives with the elimination of hydrogen bromide. The dry substances are merely heated to 100—150° without the aid of any reagent. With *p*-cresol, compounds having the following formulæ were obtained :



The use of alkalis or sodium ethoxide for effecting condensation does not seem to lose favour, and the following new applications of the method may be briefly noted. A series of unsaturated alcohols have been prepared by Faworski [1] and his collaborators by condensing phenylacetylene with ketones in presence of solid potassium hydroxide. The reaction is supposed to occur in two phases, the ketone first uniting with the caustic potash, which then interacts with the hydrocarbon :

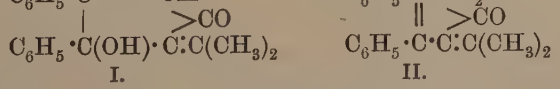
$$1.\quad >C{:}O + KOH = \quad >C<^{OH}_{OK}$$

$$2.\quad >C<^{OH}_{OK} + CH{:}C\cdot C_6H_5 = \quad >C<^{OH}_{C{:}C\cdot C_6H_5} + KOH.$$

The reaction takes place with aliphatic and aromatic ketones as well as with cyclic ketones like methyl*cyclo*hexanone, menthone, and camphor. The carbinols so formed lose the elements of water on boiling with sulphuric acid and yield new unsaturated hydrocarbons. The carbinol obtained from acetone gives the hydrocarbon $C_{11}H_{10}$ as follows :

$$CH_3\cdot C(CH_3)(OH)\cdot C{:}C\cdot C_6H_5 = CH_3\cdot C(:CH_2)\cdot C{:}C\cdot C_6H_5 + H_2O.$$

Japp and Knox [2] have continued their researches on the behaviour of benzil with ketones, substituting unsaturated for saturated ketones. With *iso*butenyl ketone, $CH_3\cdot CO\cdot CH{:}C(CH_3)_2$, in presence of potassium hydroxide, the product is a ring compound (I) which on reduction yields diphenyl*iso*propylidene*cyclo*pentenone (II) :

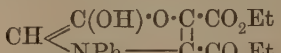


and the reaction does not, therefore, differ from that taking place with saturated ketones. In another paper by de Mouilpied,[3] cyclic structures containing nitrogen are obtained by condensing phenyl-

[1] *J. Russ. Phys. Chem. Soc.*, 1905, **37**, 643.
[2] *Trans.*, 1905, **87**, 673. [3] *Ibid.*, 435.

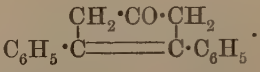
glycinoacetic esters with various compounds in presence of sodium methoxide or ethoxide. With benzaldehyde, the product is a lactone (I), with ethyl oxalate, it is a ring compound having the following formula (II):

I.

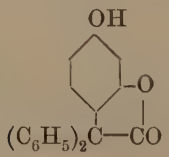


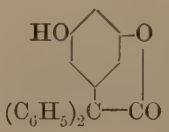
II.

The effect of changing the condensing agent and the temperature is shown in the case of benzaldehyde and acetone, which in presence of sodium hydroxide solution ordinarily yield benzylidene- and dibenzylidene-acetone. With zinc chloride at 140° in a sealed tube, Lippmann and Fritsch[1] obtained stilbene acetone and similar products with other aldehydes:



H. von Liebig[2] has studied the products obtained by fusing together benzil, resorcinol, and anhydrous sodium sulphate, and has isolated from the melt a variety of triphenylmethane derivatives, among which are compounds having the following formulæ:





Intramolecular Change.

There is perhaps no branch of organic chemistry which is more suggestive than that which deals with isomeric and other changes occurring within the molecule. Interaction between molecules has been generally conceived as the basis of chemical change, but under the same conditions parts of the same molecule may interact, and the knowledge of the mechanism of such processes cannot fail to be of the greatest value. The pinacone-pinacoline conversion is the subject this year of two investigations which have been undertaken with the object of elucidating this curious process. The change is usually represented by the wandering of an alkyl or aryl group from one carbon atom to an adjoining one and is effected by a variety of reagents. The conversion of hydrobenzoin into diphenylacetaldehyde under the action of sulphuric acid, that of benzil into benzilic acid by fused potassium hydroxide, and the formation of

[1] *Ber.*, 1905, **38**, 1626. [2] *J. pr. Chem.*, 1905, **72**, 105.

diphenylacetamide from benzildihydrocyanide recently observed by Japp and Knox[1] belong to the same category:

$$\begin{matrix} C_6H_5\cdot C(OH)\cdot CN \\ C_6H_5\cdot C(OH)\cdot CN \end{matrix} \longrightarrow \begin{matrix} (C_6H_5)_2C\cdot CN \\ C(OH)_2\cdot CN \end{matrix} \longrightarrow (C_6H_5)_2CH\cdot CO\cdot NH_2.$$

Like the majority of intramolecular changes, the process appears to be in a sense reversible, for under the influence of hydriodic acid the pinacoline passes by reduction and subsequent removal of water into the symmetrical ethylenic hydrocarbon. Couturier,[2] Delacre,[3] and Werner and Grob[4] have all observed changes of this kind.

$$(CH_3)_3C\cdot CO\cdot CH_3 \longrightarrow (CH_3)_3C\cdot CH(OH)\cdot CH_3 \longrightarrow (CH_3)_2C{:}C(CH_3)_2.$$

$$(C_6H_5)_3C\cdot CO\cdot C_6H_5 \longrightarrow (C_6H_5)_3C\cdot CH(OH)\cdot C_6H_5 \longrightarrow (C_6H_5)_2C{:}C(C_6H_5)_2.$$

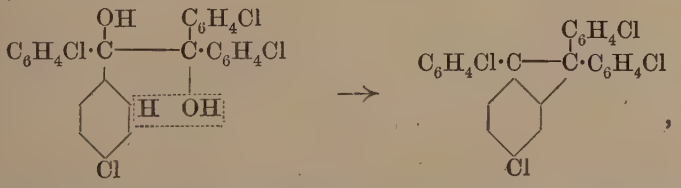
$$\begin{matrix} C_6H_4 \\ C_6H_4 \end{matrix}\!\!>\!C(C_6H_5)\cdot CO\cdot C_6H_5 \longrightarrow \begin{matrix} C_6H_4 \\ C_6H_4 \end{matrix}\!\!>\!C(C_6H_5)\cdot CH(OH)\cdot C_6H_5$$

$$\longrightarrow \begin{matrix} C_6H_4\cdot C\cdot C_6H_5 \\ C_6H_4\cdot C\cdot C_6H_5 \end{matrix}.$$

Montagne[5] has now shown that 4 : 4 : 4 : 4-tetrachlorobenzpinacone,

$$\begin{matrix} C_6H_4Cl \\ C_6H_4Cl \end{matrix}\!\!>\!C(OH)\cdot C(OH)\!<\!\begin{matrix} C_6H_4Cl \\ C_6H_4Cl \end{matrix},$$

passes into tetrachloropinacoline, which with caustic potash decomposes into *p*-chlorobenzoic acid and the same trichlorotriphenylmethane which *p*-leucaniline yields, and therefore the pinacoline contains all the chlorine atoms in the para-position. The investigation disposes of the theory that an intermediate ring compound is first formed, which would necessitate a change in the relative position of one chlorine atom:



but whether the change is preceded by the formation of an alkylene oxide, as suggested by Nef and others, is left undetermined.

A preliminary paper by Acree[6] has appeared on the same subject, but no definite results have yet been obtained. Closely related to the above is the memoir by Fourneau and Tiffeneau,[7] which describes the

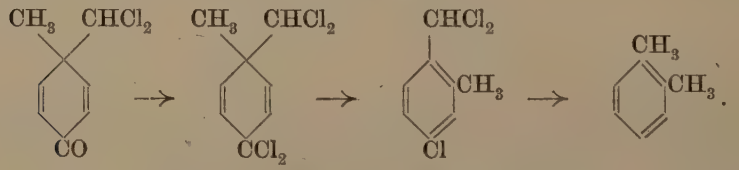
[1] *Trans.*, 1905, **87**, 681.
[2] *Ann. Chim. Phys.*, 1892, [vi], **26**, 433.
[3] *Ber.*, 1890, **23**, *ref.* 769.
[4] *Ibid.*, 1904, **37**, 2887.
[5] *Rec. trav. chim.*, 1905, **24**, 105.
[6] *Amer. Chem. J.*, 1905, **33**, 180.
[7] *Compt. rend.*, 1905, **141**, 662.

action of heat on the three series of aromatic alkylene oxides. The monosubstituted compounds of the general formula $Ar\cdot CH_2\cdot CH\cdot CH_2$ (O) give the aldehyde $Ar\cdot CH_2\cdot CH_2\cdot CHO$, the unsymmetrical disubstituted compounds $Ar\cdot C(CH_3)\cdot CH_2$ (—O—) also give the aldehyde

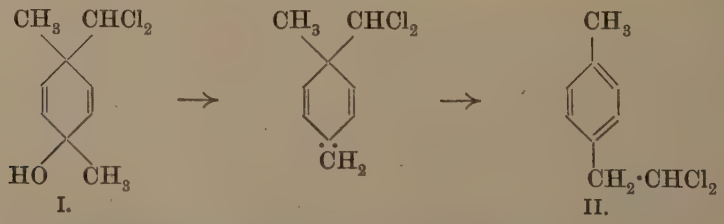
$$Ar\cdot CH(CH_3)\cdot CHO,$$

whilst the symmetrical disubstituted compounds $Ar\cdot CH\cdot CH\cdot CH_3$ (O) give the ketone $Ar\cdot CH_2\cdot CO\cdot CH_3$. A similar result has been obtained by Klages,[1] who finds that 20 per cent. sulphuric acid converts phenylmethylethylene oxide into hydratropaldehyde.

Another interesting example of intramolecular change is described by Auwers and Keil.[2] In attempting to convert 1-dichloromethyl-1-methyl-4-keto-1 : 4-dihydrobenzene into a hydrocarbon by the action of phosphorus pentachloride and subsequent reduction, they found that *o*-xylene was produced in the following way :



A change of a similar character is recorded by the same observers, who have shown that the hydrocyclic alcohol (I) readily loses water and probably passes into (II), thus :



although the formation of a bridged ring is not excluded :

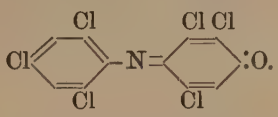
[1] *Ber.*, 1905, **38**, 1969. [2] *Ibid.*, 1693.

It was long since pointed out by Fittig[1] that the change of $\beta\gamma$- to $\alpha\beta$-unsaturated acids was reversible. A similar observation is made by Agejewa[2] in the case of β-phenylpropylene, which in presence of solid alkali forms an equilibrium mixture with symmetrical phenylmethylethylene:

$$C_6H_5\cdot CH_2\cdot CH{:}CH_2 \longrightarrow C_6H_5\cdot CH{:}CH\cdot CH_3.$$

The passage of atoms or groups from side-chain to nucleus is a common phenomenon, but Orton[3] has made the further observation that by interchanging the nitro-group in 2 : 4 : 6-tribromonitroaminobenzene the para-bromine atom is displaced:

A still more curious observation is the behaviour of the corresponding nitroamino-*s*-trichlorobenzene, which with acetic and sulphuric acids passes into *s*-trichlorophenyliminotrichlorobenzoquinone, whereby one chlorine atom changes its point of attachment,



The displacement of bromine from a hydrocarbon side-chain to the nucleus is less common. Hoering[4] has, however, shown that by the careful oxidation of anethole dibromide a ketone of the formula

$$CH_3O\cdot C_6H_3Br\cdot CO\cdot CHBr\cdot CH_3$$

is formed.

Additive Compounds.

A series of memoirs has been published by Kohler and his collaborators[5] on the behaviour of unsaturated compounds towards magnesium alkyl iodides. In the first, which appeared in 1904,[6] it was shown that reactions with compounds containing the group $-C{:}C\cdot C{:}O\cdot R$ (unsaturated aldehydes and ketones) depended on the nature of the atoms or groups associated with the ethylene carbon or CO group. The authors have extended the investigation to unsaturated esters, acid chlorides and amides, and have proved that the nature of the addition is determined by the following rules: (1) In

[1] *Annalen*, 1905, **283**, 47.
[2] *J. Russ. Phys. Chem. Soc.*, 1905, **37**, 662.
[3] *Trans.*, 1905, **87**, 389.
[4] *Ber.*, 1905, **38**, 3458.
[5] *Amer. Chem. J.*, 1905, **33**, 153, 333; 1905, **34**, 132; *Ber.*, 1905, **38**, 1203.
[6] *Amer. Chem. J.*, 1904, **31**, 642.

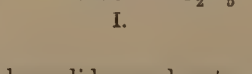
unsaturated aldehydes (R = H) the organo-magnesium compound reacts exclusively with the carbonyl group. (2) Ketones (R = CH_3) react like aldehydes. (3) Ketones (R = C_6H_5) form additive compounds in the 1 : 4-position, thus :

$$C_6H_5\cdot\overset{1}{C}H{:}\overset{2}{C}H\cdot\overset{3}{C}O\cdot\overset{4}{C}_6H_5 + C_6H_5MgBr = C_6H_5\cdot\overset{1}{C}H(C_6H_5)\cdot\overset{2}{C}H{:}\overset{3}{C}(OMgBr)\cdot\overset{4}{C}_6H_5.$$

(4) In the case of esters (R = OR), either addition occurs at the 1 : 4-position or the alkoxyl group is replaced by an alkyl group ; the first reaction occurs with aromatic and the second with aliphatic magnesium compounds. Negative groups (halogens, phenyl) in the α-position favour addition in the 1 : 4-position. With cinnamonitrile, the addition is restricted to the cyanogen group,

$$C_6H_5\cdot CH{:}CH\cdot C{:}N + C_6H_5MgBr = C_6H_5\cdot CH{:}CH\cdot C(C_6H_5)N\cdot MgBr,$$

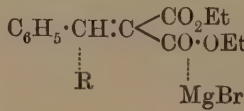
but in the α-phenyl derivative no union whatever takes place. Ethyl α-cyanocinnamate (I), which contains both conjugated systems,[1] C:C·C:O and C:C·C:N, 1 : 4-addition occurs in relation to the group C:C·C:O, for the CN group in the α-position inhibits the replacement



I.

of alkoxyl by alkyl.

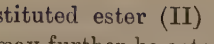
In the case of ethyl benzylidenemalonate, the following additive compound is formed (I), from which, by the action of water, the sub-



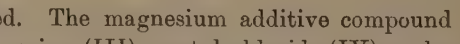
I.

II.

stituted ester (II) is obtained. The magnesium additive compound may further be acted on by bromine (III), acetyl chloride (IV), or by other halogen compounds and a variety of interesting derivatives thus



III.



IV.

prepared. Bauer[2] has also studied the behaviour of organo-magnesium compounds with unsaturated ketones of the type

$$RCH{:}CH\cdot CH{:}CH\cdot CO\cdot R^1$$

in the hope of producing a conjugated system of three double bonds, $R\cdot CH{:}CH\cdot CH{:}CH\cdot CH{:}CH\cdot R^1$, but the experiment was only partially successful, for as a rule the unsaturated alcohol and not the hydro-

[1] *Annual Report*, 1904, 105. [2] *Ber.*, 1905, **38**, 688.

carbon was formed. Thus, cinnamyleneacetophenone gave triphenylhexadienol,

$$C_6H_5\cdot CH{:}CH\cdot CH{:}CH\cdot CO\cdot C_6H_5 + C_6H_5\cdot CH_2\cdot MgCl = C_6H_5\cdot CH{:}CH\cdot CH{:}CH\cdot C(OH)\cdot C_6H_5\cdot CH_2\cdot C_6H_5.$$

Blaise and Courtot[1] have found that unsaturated esters can form additive compounds with magnesium alkyl iodides, and have prepared from methacrylic ester, dimethylpropenylcarbinol and methyl-3-pentanone. The second compound is produced by the following series of changes:

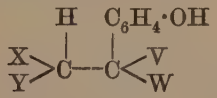
$$CH_2{:}C(CH_3)\cdot CO_2Et \longrightarrow \begin{matrix} CH_2\cdot C(CH_3)\cdot C<^{OEt}_{OMgI} \\ | \quad\quad | \\ CH_3MgI \quad CH_3 \end{matrix} \longrightarrow \begin{matrix} CH_2\cdot CH(CH_3)\cdot CO\cdot CH_3 \\ | \\ CH_3 \end{matrix}.$$

Last year's Report (p. 104) contained a passing reference to Posner's research on the combination of mercaptans with unsaturated ketones. The subject has been further studied[2] with the object of discovering if the double link in unsaturated ketones is alone responsible for the addition of the mercaptan molecule. This is answered by Posner in the affirmative.

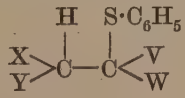
The absence of additive compounds in the case of stilbene, $C_6H_5\cdot CH{:}CH\cdot C_6H_5$, and diphenylbutadiene,

$$C_6H_5\cdot CH{:}CH\cdot CH{:}CH\cdot C_6H_5,$$

is ascribed to the number of phenyl groups which diminish the additive capacity; for both styrene, $C_6H_5\cdot CH{:}CH_2$, and phenylbutadiene, $C_6H_5\cdot CH{:}CH\cdot CH{:}CH_2$, unite with mercaptans. Posner's experience is contrary to that of Königs, who found that phenols unite with olefines by means of nuclear carbon (I), whereas Posner finds that in the case of mercaptans addition takes place through the sulphur atom (II).



I.



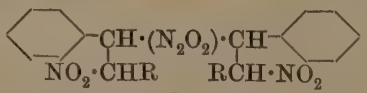
II.

Ruhemann,[3] who has been engaged in a similar line of research, points out that in presence of sodium ethoxide or piperidine, olefinic ketones form additive compounds with one molecule of mercaptan, and has corrected previous observations of Posner in which two molecules are described as entering into combination. Benzylideneacetophenone and *iso*amyl mercaptan give *iso*amylthiolbenzylaceto-

[1] *Compt. rend.*, 1905, **140**, 370. [2] *Ber.*, 1905, **38**, 646.
[3] *Trans.*, 1905, **87**, 17, 461.

phenone, $C_6H_5 \cdot CH(S \cdot C_5H_{11})CH_2 \cdot CO \cdot C_6H_5$. Similar additive products were prepared from benzylidenedeoxybenzoin, ethyl benzylidenebenzoylacetate, and cinnamylideneacetophenone by union with phenyl mercaptan. Triolefinic ketones combine with one or two molecules of mercaptan, and acetylenic ketones also yield additive compounds.

Bauer,[1] in extending his researches on the behaviour of unsaturated compounds towards bromine, shows that the difficulty of addition is increased by the presence of cyanogen as well as by phenyl and ester groups in the following order : $C_6H_5 \longrightarrow CO_2R \longrightarrow CN$, which is also the order determining the dissociation constant ; that is to say, the more strongly negative the groups attached to the ethylene carbon, the less readily does bromine combine. The introduction of nitro-groups into the phenyl complex also diminishes the additive power for bromine by increasing the negative character of the nucleus. Zincke and Mühlhausen[2] conclude, from the behaviour of dry hydrogen bromide on aldehydes, ketones, and unsaturated ketones, that additive power is a function of the molecule as a whole and not of individual constituents. Neither a double bond nor a ketone group alone can induce combination, which only occurs when, in addition to the ketone group, a double bond or OH or OR group is present. Benzophenone, for example, forms no additive compound, whereas *pp*-dihydroxybenzophenone does. This is merely stating in other words that positive groups increase the additive power for acids, a fact which has already been demonstrated by Baeyer and Villiger and others. Vorländer and his collaborators[3] have made a very comprehensive study of the additive compounds of $\alpha\beta$-unsaturated ketones with acids and salts and lay down certain theoretical conclusions which cannot be conveniently condensed. Before concluding our account of the behaviour of unsaturated compounds, attention should be drawn to the paper of Wieland and Bloch[4] who have shown that the formation of additive compounds of nitrogen trioxide with phenylethylenes having the formula $C_6H_5 \cdot CH{:}CHR$ are subject to certain conditions. If R is positive, dimolecular pseudonitrosites are formed (I) :



I.

If, on the contrary, R is negative, as in unsaturated ketones and aldehydes, the groups NO and NO_2 form saturated unimolecular compounds. Thus, benzylideneacetone and benzylideneacetophenone yield no

[1] *Ann. Reports*, 1904, 103 ; *J. pr. Chem.*, 1905, [ii], **72**, 201.
[2] *Ber.*, 1905, **38**, 466.
[3] *Annalen*, 1905, **341**, 80.
[4] *Ibid.*, **340**, 63.

nitrosites unless a strongly positive group is present in the benzene nucleus as in the anisylidene derivatives.

Nitrogen tetroxide combines with unsaturated ketones of the type $ArC{:}C{\cdot}CO{\cdot}R$ to form in the first instance compounds of the formula (I) which, however, are very unstable and readily lose nitrous acid, passing into unsaturated nitroketones (II):

$$\begin{array}{l} Ar{\cdot}CH\text{——}CH{\cdot}CO{\cdot}R \\ \quad\;\; | \qquad\;\; | \\ \quad O{\cdot}NO \quad NO_2 \end{array} \qquad \text{I.}$$

$$\begin{array}{l} Ar{\cdot}CH{:}C{\cdot}CO{\cdot}R \\ \qquad\;\; | \\ \qquad NO_2 \end{array} \qquad \text{II.}$$

These nitro-compounds can be hydrolysed by an ethereal solution of ammonia into aldehydes or ketones (ketonic hydrolysis) (III), whilst caustic soda produces acid hydrolysis (IV):

$$Ar{\cdot}CHO + CH_2(NO_2){\cdot}CO{\cdot}R \qquad \text{III.}$$

$$Ar{\cdot}CH{:}CH{\cdot}NO_2 + RCO{\cdot}OH \qquad \text{IV.}$$

By the ketonic hydrolysis of anisylidenenitroacetone, nitroacetone, $CH_2(NO_2){\cdot}CO{\cdot}CH_3$, has been obtained.

Meisenheimer and Heim[1] find that phenylnitroethylene and sodium methoxide react according to the equation:

$$C_6H_5{\cdot}CH{:}CH{\cdot}NO_2 + NaOCH_3 = C_6H_5{\cdot}CH(O{\cdot}CH_3)CH{:}NO{\cdot}ONa.$$

Unsaturated Hydrocarbons.

Very little fresh light has been thrown on the constitution of triphenylmethyl since the last report was published (p. 105). The most important contribution to the subject is undoubtedly that of Tschitschibabin,[2] which appeared towards the close of the year. The identity of the bimolecular triphenylmethyl with hexaphenylethane was disproved by the supposed synthesis of the latter by Ullmann and Borsum,[3] which was found to be a stable compound of entirely distinct properties. An investigation into the structure of Ullmann's synthetical compound by Tschitschibabin has led to the interesting discovery that the substance in question is not hexaphenylethane, but in all probability a compound having the formula

$$(C_6H_5)_3C{\cdot}C_6H_4{\cdot}CH(C_6H_5)_2.$$

This structure seems to follow from its behaviour with bromine, which converts it into a monobromo-derivative, and from the action of water and pyridine on the latter compound, which transforms it into the carbinol:

$$(C_6H_5)_3C{\cdot}C_6H_4{\cdot}CBr(C_6H_5)_2 + H_2O = (C_6H_5)_3C{\cdot}C_6H_4{\cdot}C(OH)(C_6H_5)_2 + HBr.$$

[1] *Ber.*, 1905, **38**, 466.
[2] *Ibid.*, 1904, **37**, 4709.
[3] *Ibid.*, 1902, **35**, 2877.

Tschitschibabin[1] concludes that Gomberg's compound may still be hexaphenylethane, and explains its conversion into the above hydrocarbon by a disruption and reunion of the molecule in the following way:

$$(C_6H_5)_3C\cdot C(C_6H_5)_3 + HCl = (C_6H_5)_3CH + (C_6H_5)_3CCl = (C_6H_5)_3C\cdot C_6H_4\cdot CH(C_6H_5)_2 + HCl.$$

The only new contribution by Gomberg is a paper in conjunction with Cone,[2] describing a series of additive compounds of triphenylmethyl with different esters and hydrocarbons. The former are crystalline substances having the general formula $2(C_6H_5)_3C + 1$ mol. of ester, to which the authors assign the following structure:

$$\begin{matrix} RCO \\ R^1 \end{matrix}\!\!>\!O\!<\!\!\begin{matrix} C(C_6H_5)_3 \\ C(C_6H_5)_3 \end{matrix}.$$

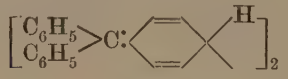
The additive compounds with the hydrocarbons are similarly composed of 2 molecules of triphenylmethyl with 1 molecule of the hydrocarbon (ethylbenzene and the three isomeric xylenes). Triphenylmethyl combines also with fractions of light petroleum, carbon disulphide, and unsaturated hydrocarbons like amylene, yielding in the latter case the compound $2(C_6H_5)_3C + C_5H_{10}$. It also unites with ketones (I) (except acetone), ethers (II), and certain nitriles (III), but aldehydes and acetonitrile are indifferent. They all retain their unsaturated character. The formulæ of these compounds is represented as follows:

$$\begin{matrix} R \\ R^1 \end{matrix}\!\!>\!C\!:\!O\!<\!\!\begin{matrix} C(C_6H_5)_3 \\ C(C_6H_5)_3 \end{matrix} \qquad \text{I.}$$

$$\begin{matrix} R \\ R^1 \end{matrix}\!\!>\!O\!<\!\!\begin{matrix} C(C_6H_5)_3 \\ C(C_6H_5)_3 \end{matrix} \qquad \text{II.}$$

$$C_2H_5\cdot C\!:\!N\!<\!\!\begin{matrix} C(C_6H_5)_3 \\ C(C_6H_5)_3 \end{matrix}. \qquad \text{III.}$$

At the close of the paper the authors review the evidence of Tschitschibabin and the alternative formulæ suggested by Heintschel (IV) and Jacobson (V):



IV.

V.

Most of the arguments based on the unsaturated character of the hydrocarbon and the property of forming additive compounds are reaffirmed in support of the original formula.

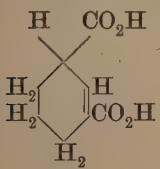
[1] *Ber.*, 1905, **38**, 771. [2] *Ibid.*, 1333.

Hydrocyclic Compounds.

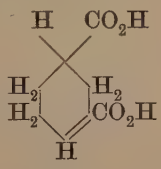
The number of individual memoirs which have appeared in the course of the year on the preparation and properties of this group of compounds is very large, but the methods used in their preparation offer very little novelty. Some of these methods may be illustrated by reference to the following more important investigations.

The reduction of benzene derivatives by the method of Sabatier and Senderens has been employed in the preparation of *cyclo*hexane, *cyclo*hexanol and their derivatives,[1] in the preparation of thymomenthol from thymol,[2] of the three methyl*cyclo*hexanols and hexanones from the isomeric cresols,[3] of decahydro-β-naphthol and octohydronaphthalene,[4] and of hexa- and octo-hydrophenanthrenes.[5]

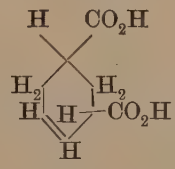
Another reduction method is illustrated by a paper of considerable interest by Perkin and Pickles,[6] containing an account of the four isomeric tetrahydro*iso*phthalic acids which Baeyer and Villiger were unsuccessful in obtaining. Two of these substances were formed by the reduction of *iso*phthalic acid by sodium and alcohol, and separated by utilising the different solubilities of the calcium salts. The other two were prepared indirectly from them. The series is represented as follows:



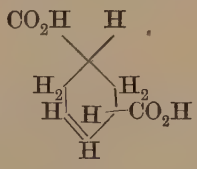
Δ^2 (m. p. 168°).



Δ^3 (m. p. 244°).

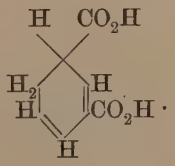


cis-Δ^4 (m. p. 165°).



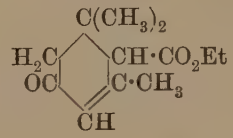
trans-Δ^4 (m. p. 227°).

No dihydro*iso*phthalic acid was obtained in this way, but one member was subsequently prepared from 3 : 4-dibromohexahydro*iso*phthalic acid (from the bromination of the hexahydro-compound) by the removal of hydrogen bromide, to which the following constitution is provisionally assigned :

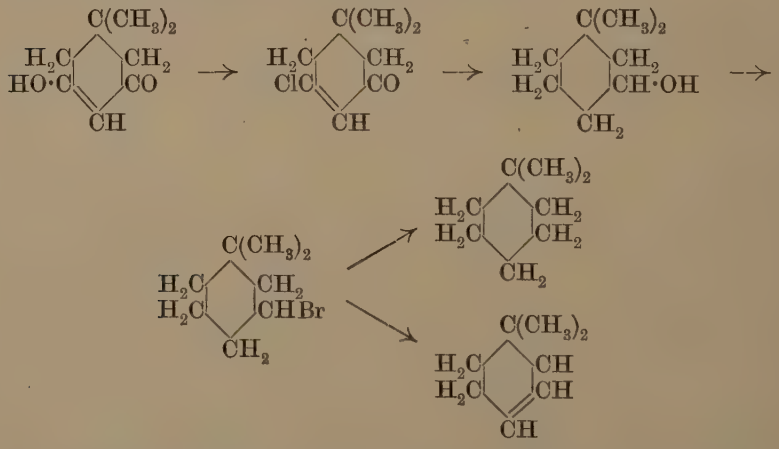


[1] Freundler and Damond, *Compt. rend.*, 1905, **141**, 593.
[2] Brunel, *ibid.*, 1905, **140**, 252.
[3] Sabatier and Mailhe, *ibid.*, 350 ; **141**, 20.
[4] Leroux, *ibid.*, **140**, 59 ; **141**, 46.
[5] Breteau, *Compt. rend.*, 1905, **141**, 942.
[6] *Trans.*, 1905, **87**, 293, 841.

Among the synthetical methods may be mentioned the condensation of ethyl *iso*propylideneacetoacetate and ethyl sodioacetoacetate, described by Merling[1] as a δ-ketone ester having the formula

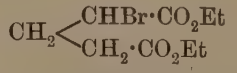


Crossley[2] has obtained from 1 : 1-dimethyldihydroresorcin, which is also a condensation product, 1 : 1-dimethylhexahydrobenzene and 1 : 1-dimethyl-Δ^3-tetrahydrobenzene. The original compound is treated first with phosphorus trichloride and then reduced to the alcohol. With hydrobromic acid, the bromide is obtained, which, on treatment with zinc dust in aqueous alcoholic solution, gives hexahydrobenzene, and with alcoholic potash the unsaturated hydrocarbon :



The 1 : 1-dimethylhexahydrobenzene is not identical with the hydrocarbon obtained by Zelinsky and Lepeschkin[3] from camphoric acid.

The synthesis of a trimethylene derivative is recorded by Perkin and Tattersall by the action of alcoholic potash on α-bromoglutaric ester :[4]

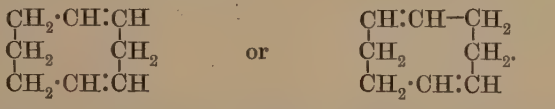


One of the most interesting of the methods recently introduced for obtaining hydrocyclic compounds is an adaptation by Willstätter of Hofmann's method of exhaustive methylation for removing nitrogen

[1] *Ber.*, 1905, **38**, 979.
[2] *Trans.*, 1905, **87**, 1487.
[3] *Annalen*, 1901, **319**, 303.
[4] *Trans.*, 1905, **87**, 362.

from the ring in breaking down the alkaloids. Hofmann obtained in this way unsaturated hydrocarbons of the aliphatic series. The discovery of tropilidine by Merling among the fragments of the tropine molecule and its identification with the *cyclo*heptadiene derived from suberone prepared the way for Willstätter's brilliant achievement of the synthesis of tropidine and atropine.[1]

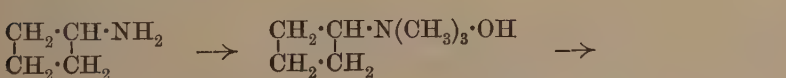
Willstätter and Veraguth[2] have now succeeded in breaking up the alkaloid pseudopelletierine from pomegranate rind into an eight-membered carbon ring, *cyclo*octadiene, C_8H_{12}, by a process similar to that which gave *cyclo*heptadiene. The position of the double bond is still undetermined, but the hydrocarbon has probably one or other of the following alternative formulæ:



In consequence of the great resistance offered by the substance to further dehydrogenation, the authors have not yet succeeded in producing a *cyclo*octatetraene, which would possess a peculiar interest from its structural analogy with benzene.

*cyclo*Octadiene shows a great tendency to polymerise; this change occurs on heating, with explosive violence, the substance passing into a well-crystallised di*cyclo*octadiene. Towards permanganate, the hydrocarbon is very unstable, and it also reacts readily with bromine. In these respects it differs from Doebner's compound,[3] which was obtained from vinylacrylic acid by distillation with baryta, and on the structure of which the authors throw considerable doubt. In the tendency to polymerise, *cyclo*octadiene resembles Para caoutchouc (p. 126), which Harries represents as a polymeric dimethyl derivative of the same hydrocarbon.

The method of exhaustive methylation which has been found so serviceable in obtaining unsaturated ring compounds with seven and eight carbon atoms has been applied by Willstätter[4] to the preparation of *cyclo*butadiene from Perkin's[5] amino*cyclo*butane by the following series of changes:



[1] *Annalen*, 1901, **317**, 204; 1903, **326**, 1.
[2] *Ber.*, 1905, **38**, 1975.
[3] *Ibid.*, 1902, **35**, 2129, 2538; 1903, **36**, 4318.
[4] *Ibid.*, 1905, **38**, 1992.
[5] *Trans.*, 1894, **65**, 950.

The process does not go smoothly, for in addition to *cyclo*butene a certain amount of 1 : 3-butadiene is formed by the opening of the ring

$$\begin{matrix} CH_2{:}CH \\ | \\ CH_2{:}CH \end{matrix}$$

Before closing our review of the synthesis of hydrocyclic compounds, reference must be made to the xanthogenic reaction of Tschugaeff for converting cyclic alcohols into unsaturated hydrocarbons. The process may be illustrated by the formation of $\gamma\delta$-methyl*cyclo*hexene from β-methyl*cyclo*hexanol, which has been investigated by Markownikoff and Stadnikoff.[1]

The *cyclo*hexanol dissolved in xylene is first heated with sodium, after which carbon disulphide and methyl iodide are added. The product is a xanthogenic ester which, on heating, breaks up into the hydrocarbon, methyl mercaptan, and carbonyl sulphide :

$$CH_3{\cdot}C_6H_{10}{\cdot}CS{\cdot}S{\cdot}CH_3 + O = C_7H_{12} + CH_3{\cdot}SH + COS.$$

The change from alcohol to hydrocarbon is represented as follows :

$$\begin{matrix} CH_2{\cdot}CH_2 & \text{———} & CH{\cdot}OH \\ | & & | \\ CH_2{\cdot}CH(CH_3){\cdot}CH_2 & & \end{matrix} \longrightarrow \begin{matrix} CH_2{\cdot}CH & \text{=====} & CH \\ | & & | \\ CH_2{\cdot}CH(CH_3){\cdot}CH_2 & & \end{matrix}.$$

The removal of water from hydrocyclic alcohols can also be effected by heating with potassium hydrogen sulphate, a method which is described by Perkin in his synthesis of the terpenes (p. 123) and by Brunel [2] in the preparation of *cyclo*hexane from *cyclo*hexanol.

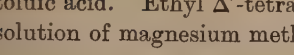
Terpenes and Camphor.

The methods which W. H. Perkin, jun., applied so successfully to the synthesis of terpineol and dipentene, an account of which appeared in last year's Report (p. 117), have since been extended with slight variation to the synthesis of similar compounds. Perkin, in conjunction with Pickles, Matsubara, Kay, and Tattersall,[3] has obtained a series of menthenols, menthadienes, menthanols, and menthanes.

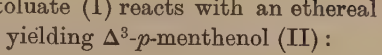
The menthenols and menthanols usually possess the peppermint odour of terpineol, whilst that of the menthadienes resembles the characteristic lemon smell of dipentene. One example of the method employed in the preparation of these substances must suffice. The starting point is the ester of a tetrahydrotoluic acid, which is usually obtained by removing hydrogen bromide from a bromohexahydro-

[1] *Annalen*, 1905, **336**, 310.
[2] *Bull. Soc. chim.*, 1905, [iii], **33**, 270.
[3] *Trans.*, 1905, **87**, 639, 661, 1066, 1083.

toluic acid. Ethyl Δ'-tetrahydro-*p*-toluate (I) reacts with an ethereal solution of magnesium methyl iodide yielding Δ^3-*p*-menthenol (II):



I.

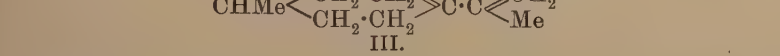


II.

On digesting the latter with potassium hydrogen sulphate, water is removed and $\Delta^{3:8:9}$-*p*-menthadiene is formed (III):

III.

The new terpene differs in many important characters from dipentene, more especially in the fact that it combines with only one molecule instead of two molecules of bromine, hydrochloric and hydrobromic acids. This is ascribed to the presence of a conjugated system of double linkings, C:C·C:C, in which bromine is known to unite only with the end carbon atoms, forming the group CBr·C:C·CBr.[1] By a similar series of reactions to the above, using ethyl hexahydro-*p*-toluate, *p*-menthanol (IV) and Δ^8-*p*-menthene (V) were prepared:



IV. V.

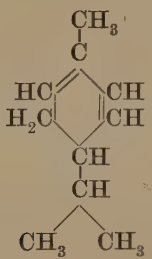
Finally, from the latter (V), *p*-menthane (hexahydrocymene) was obtained by reducing the additive compound of *p*-menthene with hydrobromic acid, $C_{10}H_{18}$,HBr, with zinc dust and acetic acid. Similar reactions have been carried out with the esters of hexa- and tetra-hydrobenzoic acids, hexa- and tetra-hydro-*o*-toluic acids, and hexa- and tetra-hydro-*m*-toluic acids.

Haller and Martini[2] describe a synthesis of menthene and menthol from methyl*cyclo*hexanone by the use of sodamide. A sodium derivative is thus obtained, which, with *iso*propyl iodide, yields menthone, and the latter on reduction is converted into menthol. By a similar process, β-methyl*cyclo*hexanone is converted into homologues of menthol and menthone, and a series of alkyl derivatives of thujone has been obtained by using sodamide in the same way.[3] A second synthesis of menthone and menthol by the action of reduced nickel and hydrogen on pulegone is described by the same authors.[4]

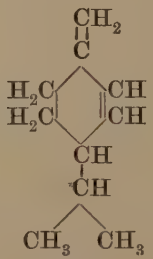
In the year 1904, Wallach published a very complete investigation on the nature of phellandrene, and pointed out that in addition to ordinary or α-phellandrene (found as dextro-enantiomorph in elemi and bitter fennel oil and as lævo-compound in Australian eucalyptus)

[1] *Ann. Reports*, 1904, 105.
[2] *Compt. rend.*, 1905, **140**, 130.
[3] *Ibid.*, 1626.
[4] *Ibid.*, 1298.

a second or β-phellandrene is present in *Phellandrium aquaticum*. The first was shown to have the structure of $\Delta^{2:5}$-dihydrocymene (I) by the conversion of nitrophellandrene into active menthenone (carvotanacetone), whilst β-phellandrene, which forms the subject of a subsequent investigation by Wallach,[1] is shown to possess the formula (II):



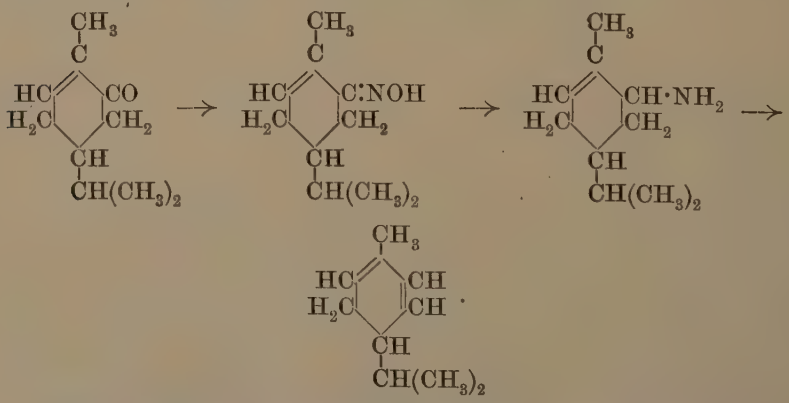
I.



II.

Harries and Johnson[2] have now confirmed the formula given to α-phellandrene by the reverse process to that used by Wallach, namely, by converting *d*-menthenone into phellandrene by the following steps.

Menthenone is first treated with phosphorus pentachloride and the resulting chloride converted into chlorophellandrene by boiling with quinoline. The chlorophellandrene on reduction with zinc dust in methyl alcohol yields α-phellandrene. Another and better method is to reduce menthenoneoxime to Δ^6-menthenamine and to distil the product under diminished pressure with phosphoric acid.

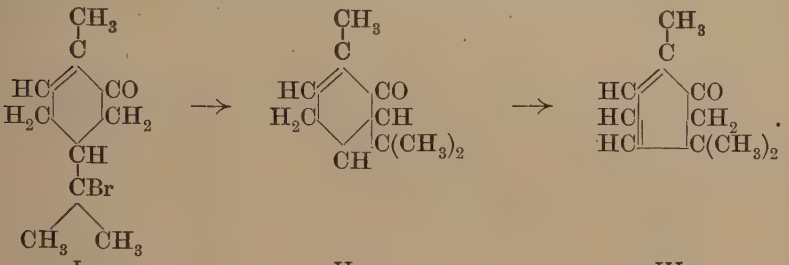


Wallach and Böcker[3] have studied the various sources of thujone and definitely show that three isomeric ketones exist, which they distinguish as α-, β-, and γ-thujones.

Wallach and Köhler[4] throw doubt on Baeyer's formula for eucarvone

[1] *Annalen*, 1905, **340**, 1. [2] *Ber.*, 1905, **38**, 1832.
[3] *Annalen*, 1905, **336**, 247. [4] *Ibid.*, **339**, 94.

(II), which is obtained from carvone hydrobromide (I) by removal of hydrogen bromide. Certain anomalies which the substance in question exhibits are removed if, in place of Baeyer's bridged ring formula, a seven-ring structure (III) is substituted. Baeyer's formula will then represent an intermediate phase in the process of preparation.



I. II. III.

Tilden and Burrows,[1] and also Leach,[2] have studied the action of potassium cyanide on an alcoholic solution of the nitrosochlorides of certain terpenes. Pinene and limonene yield nitrosocyanides of the formula $C_{10}H_{15}(:NOH)\cdot CN$, which can be hydrolysed, and yield the corresponding amides and acids.

Forster and Fierz [3] have shown that by the action of potassium cyanate on the hydrochloride of aminocamphor, a carbamide, isomeric with the one obtained by Rupe, is formed, which they term camphoryl-ψ-carbamide, having the formula

$$C_8H_{14}\begin{cases}CH\text{——}NH\\ C(OH)\cdot NH\end{cases}CO.$$

They find that Rupe's compound undergoes conversion into the new isomeride by shaking it with sodium hydroxide solution and that the converse change is effected by dilute hydrochloric acid. They therefore assign to Rupe's carbamide the formula

$$C_8H_{14}\begin{cases}CH\cdot NH\cdot CO\cdot NH_2\\ CO\end{cases}.$$

Whilst Rupe's carbamide gives with nitrous acid camphorylcarbimide, the pseudo-compound forms a nitroso-compound which, on reduction, yields camphorylsemicarbazide. This substance is optically active and can be usefully applied to the preparation of active carbazones. The pseudo-carbazide, by the further action of nitrous acid, is converted into camphorylazoimide :

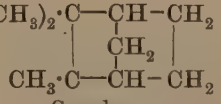
$$C_8H_{14}\begin{cases}CH\cdot N(NH_2)\\ C(OH)\text{—}NH\end{cases}CO + HNO_2 = C_8H_{14}\begin{cases}CH\cdot N_3\\ CO\end{cases} + HNCO + H_2O.$$

[1] *Trans.*, 1905, **87**, 344. [2] *Ibid.*, 413. [3] *Ibid.*, 110, 722.

The use of the xanthogenic ester reaction of Tschugaeff has already been noticed (p. 122). A long and interesting memoir is contributed by Tschugaeff [1] on the subject, in which he describes how the reaction may be applied to the preparation of pure esters of the alcohols of the terpene and camphor series and to the unsaturated hydrocarbons derived from them.

A passing reference was made in last year's Report (p. 92) to the action of ozone in breaking down the caoutchouc molecule, which was the subject of a memoir by Harries.[2] This investigation has since been extended and from the nature of the products of decomposition Harries proposes the following formula for Para caoutchouc :

The arguments adduced in its favour would occupy too much space to consider in detail, and the reader is referred to the original memoir. The reader's attention is also directed to an important paper by Moycho and Zienkowski,[3] in which they bring evidence in favour of Wagner's formula for camphene from a study of its decomposition products :



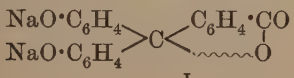
Camphene.

Colour and Structure.

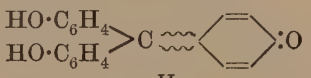
In the former report (p. 123), the views of Baeyer and Villiger on the constitution of the triphenylmethane colours was discussed and it was then stated that the authors had arrived at the conclusion that these colouring matters were to be represented by the quinonoid structure. A further study of the subject has disclosed a difficulty,[4] inasmuch as the sulphates of *p*-trichloro- and *p*-tri-iodo-triphenylcarbinols are highly coloured salts (the latter closely resembles fuchsine) which show no tendency to lose halogen. This seems scarcely compatible with a quinonoid structure, for the chlorine of the quinone nucleus should be easily detached by the action

[1] *J. Russ. Phys. Chem. Soc.*, 1905, **36**, 988.
[2] *Ber.*, 1905, **38**, 1195.
[3] *Annalen*, 1904, **340**, 17 ; *Ber.*, 1905, **38**, 2461.
[4] *Ber.*, 1905, **38**, 569, 1156.

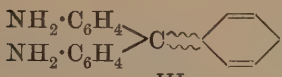
of silver nitrate solution, and this is not the case. Adopting a view held by Walden and Gomberg, that the yellow solutions with which triphenylmethyl chloride dissolves in certain solvents are due to dissociation, Baeyer introduces a distinction between an ionisable and non-ionisable valency by the use of a zigzag line, which marks the ionisable bond. In the case of the triphenylmethane derivatives, this ionisable bond is called the carbonium bond, and is responsible for the colour, whilst the other kind of attachment, which is represented by an ordinary straight bond, produces no colour. But it must not be supposed that electrolytic dissociation has anything in common with the new theory, since the parts of a compound which are not known to dissociate may be attached by zigzag bonds to denote their colour. The following are some of the new formulæ: (I) is the sodium salt of phenolphthalein; (II) that of aurin; (III) that of Homolka's colour base; and (IV) that of azo-compounds:



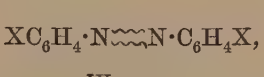
I.



II.

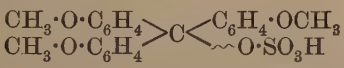


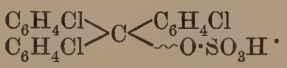
III.



IV.

whilst the coloured sulphates of trianisyl- and trichlorophenyl-carbinol appear thus:





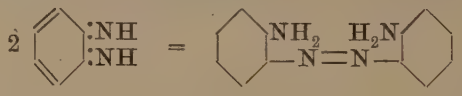
It may be expedient to draw distinctions between the two kinds of attachment in order to denote colour or its absence, but one is tempted to ask whether such distinctions embody any new conception or explanation of the phenomenon.

A reference was made in last year's Report (pp. 122, 123) to the new quinones and iminoquinones obtained by Willstätter and his collaborators. This series of interesting compounds has been increased by the addition of the quinones and quinoneimines derived from *p*-dimethylphenylenediamine, *o*-phenylenediamine, *p*-dihydroxydiphenyl, and benzidine.[1] These substances are obtained by the former method of oxidation in an inert solvent with silver oxide or lead peroxide. Diphenoquinone, $O{:}C_6H_4{\cdot}C_6H_4{:}O$, crystallises in two modifications, one resembling chromic acid in appearance and the other consisting of colourless needles. The first can be converted into the second. The substance is without smell, is non-volatile, and is decomposed by alkalis, acids, and even by water alone. Diphenylquinonedi-imine,

[1] *Ber.*, 1905, **38**, 1232, 2244, 2348.

$NH{:}C_6H_4{\cdot}C_6H_4{:}NH$, crystallises in reddish-brown needles; quinonedimethylimine, $CH_3{\cdot}N{:}C_6H_4{:}N{\cdot}CH_3$, shows a close resemblance to quinone di-imine. In the crystalline form it is colourless, but in solution it possesses a yellow colour, which, however, differs in character from that of the hydrochloride.

Quinonemonomethylimine, $CH_3{\cdot}N{:}C_6H_4{:}O$, was obtained, but as it explodes in the free state no analysis could be performed. The author draws a distinction between the coloured and colourless derivatives by using Baeyer's carbonium bond. By the oxidation of *o*-phenylenediamine in ether, a solution was obtained which appeared pale yellow by transmitted light and reddish-yellow by reflected light, resembling the solution of pure *o*-benzoquinone. The solution stains the skin black, and, on evaporation of the ether in a vacuum, the substance changes rapidly. On warming the ethereal solution or on shaking it with hydrochloric acid, two compounds are formed, one of which is the well-known diaminophenazine and the other *o*-azoaniline. The latter is probably formed by the polymerisation of the di-imine:



J. B. Cohen.

ORGANIC CHEMISTRY—HETEROCYCLIC DIVISION.

During the last twenty or thirty years the progress of synthetical organic chemistry has been so great that at the present time we are acquainted with compounds possessing heterocyclic structures of great variety. Whereas the chief interest in former decades was the production of rings of new type, the present tendency is more in the direction of a closer examination of known ring structures with a view to elucidating on the one hand the mechanism of ring-formation, on the other that of the transformation of rings, it may be into other rings, made up of a different number of atoms, or differing from the original ring in the arrangement of linkages, the latter change frequently accompanying the production of salts.

At the same time, new compounds of familiar type are continually being discovered, either by known processes or by new synthetical methods, whilst occasionally new types of ring make their appearance.

But, in addition to the work which appeals more directly to the chemist, there is that branch connected more closely with animal and vegetable physiology aiming at the determination of the structure of naturally occurring products, so that now no year passes in which some addition is not made to our knowledge of the alkaloids, the substances of the uric acid group, and the natural colouring matters.

Mechanism of Ring-formation.

By far the greater number of cyclic compounds contain five or six members to the ring. In the case of substances possessing homocyclic structure, the "Spannungs-Theorie" of Von Baeyer[1] gives a plausible explanation of the preferential formation of such compounds, and it would appear that the replacement of carbon atoms by atoms of other elements has generally little influence on the greater stability of five- and six-membered rings. But whilst ring compounds with a greater or less number of atoms in the ring have been met with amongst homocyclic compounds, so also the same obtains with heterocyclic substances. For the solution of problems in connection with the

[1] *Ber.*, 1885, **18**, 2277.

possible size of closed rings, substances containing amino-groups seem especially suitable on account of the great reactivity of nitrogen when in this condition.

Heterocyclic compounds with rings of more than six members have been obtained by J. von Braun[1] alone and in conjunction with A. Steindorff.[2] ω-Chloro-*N*-hexylamine and ω-chloro-*N*-heptylamine isomerise to the hydrochlorides of hexamethyleneimine and heptamethyleneimine. The first base boils between 120° and 130° and smells like piperidine, but its formation is not so smooth as that of the latter substance, a large amount of a polymeride being formed. This polymeric hexamethyleneimine appears to be a di-secondary base, and its carbon and nitrogen atoms probably form a 14-membered ring,

$$NH<\begin{matrix}(CH_2)_6\\(CH_2)_6\end{matrix}>NH.$$

Compounds with rings of seven members have also been obtained by Wölbling[3] and Lieck[4] by the action of hydrazine on β-deoxybenzoin-*o*-carboxylic acid or its lactone (that is, 3-phenyl*iso*coumarin) and *m*-tolyl*iso*coumarin respectively. The compounds formed might possess either of the following structures :

$$C_6H_4<\begin{matrix}CH_2\text{——}C\cdot C_6H_5\\CO\cdot NH\cdot N\end{matrix} \quad \text{or} \quad C_6H_4<\begin{matrix}CH{:}C\cdot C_6H_5\\CO\text{–}N\cdot NH_2\end{matrix},$$

but since substances undoubtedly of the second type are produced by the isomerisation (similar to the Beckmann transformation) of the original condensation products, these must have the seven-membered ring structure.

S. Gabriel[5] finds that ω-homopropylphthalimide hydrolysed by potassium hydroxide gives the aminopropyl ester of phthalic acid. The transformation is explained by the following scheme :

$$C_6H_4<\begin{matrix}CO\\CO\end{matrix}>N\cdot CH_2\cdot CH_2\cdot CH_2Br \longrightarrow C_6H_4<\begin{matrix}CO\cdot NH\cdot C_3H_6Br\\CO_2K\end{matrix} \longrightarrow$$

$$C_6H_4<\begin{matrix}CO\cdot NH\cdot CH_2\\CO\text{—}O\text{—}CH_2\end{matrix}>CH_2 \longrightarrow C_6H_4<\begin{matrix}CO_2H\\CO\cdot O\cdot C_3H_6\cdot NH_2\end{matrix}.$$

The intermediate nine-membered ring compound is not simply hypothetical, it has been isolated, as has also the corresponding eight-membered ring compound from β-bromoethylphthalimide; these substances have been characterised by their nitroso-derivatives. Gabriel[6] at the same time prepared the nitroso-derivative of hydroxyethyl-

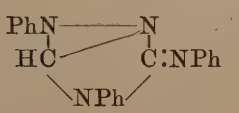
[1] *Ber.*, 1905, **38**, 964, 2340. [2] *Ibid.*, 3083. [3] *Ibid.*, 3845.
[4] *Ibid.*, 3853. [5] *Ibid.*, 2389. [6] *Ibid.*, 2405.

carbamic anhydride, notable in that it spontaneously decomposes, largely in accordance with the equation

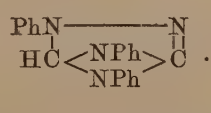
$$CO\begin{cases}N(NO)\cdot CH_2\\ O\text{———}CH_2\end{cases} = CO_2 + N_2 + H_2O + C_2H_2.$$

Some new bridged-ring compounds with elements besides carbon in the nucleus have been discovered in the past year. On account of their interesting properties the *endo*iminodihydrotriazoles discovered by M. Busch [1] deserve mention. Triphenylaminoguanidine, obtained by the action of lead oxide on a mixture of phenylhydrazine thiocarbanilide, or aniline and diphenylthiosemicarbazide, condenses with formic acid.

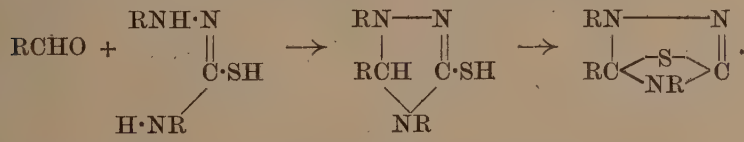
$$CH_2O_2 + \begin{matrix}C_6H_5\cdot NH\cdot NH\\ C_6H_5\cdot NH—C:N\cdot C_6H_5\end{matrix} \longrightarrow$$



or



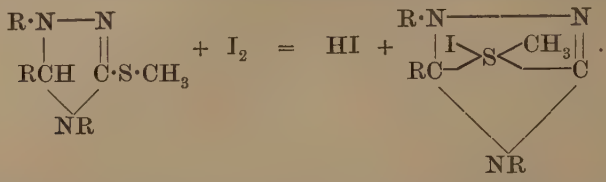
The second formula, that of 1 : 4-diphenyl-3 : 5-*endo*anilinodihydrotriazole, is preferred. The nitrate of the base (called shortly *nitron*) is so insoluble that nitrates may be gravimetrically estimated with its help (*loc. cit.*, p. 861). In a later paper, conjointly with G. Mehrtens,[2] it is shown that formaldehyde and subsequent oxidation may replace the formic acid; this leads one to formulate the products obtained from β-thiosemicarbazides and aldehydes [3] as *endo*thiodihydrotriazoles.



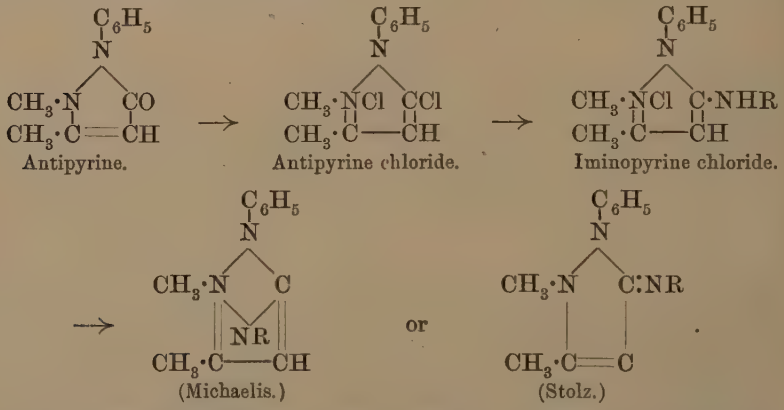
*endo*Iminodihydrotriazoles yield quaternary ammonium iodides, and these give pseudo-bases on treatment with alkalis.

[1] *Ber.* 1905, **38**, 856. [2] *Ibid.*, 4049.
[3] *J. pr. Chem.*, 1903, [ii], **67**, 201.

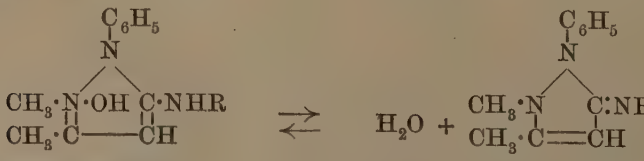
From thiodihydrotriazoles, *endo*sulphonium iodides may be obtained.



According to A. Michaelis[1] somewhat similarly constituted bridged-rings occur in the "pyrines," which result from the action of primary bases on antipyrine chloride.[2] F. Stolz,[3] however, considers the products to be imino-compounds.

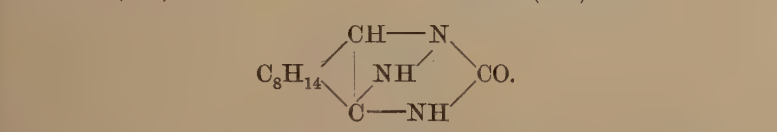


The bases obtained are usually soluble in water with alkaline reaction, whence Michaelis considers his view of the constitution correct, notwithstanding the fact that he obtained a different substance, starting with antipyrine and finally reacting with *p*-bromoaniline ($R = C_6H_4Br$), from the one which he obtained from bromoantipyrine and final condensation with aniline ($R = C_6H_5$). Stolz pointed out that the production of the same or different products should decide as to the correctness of the first or second (Stolz's) formula, and Michaelis's formulation of the free iminopyrine as an internal salt is certainly somewhat improbable. The solubility in water and alkaline reaction is far more probably to be accounted for by an equilibrium in the following sense :

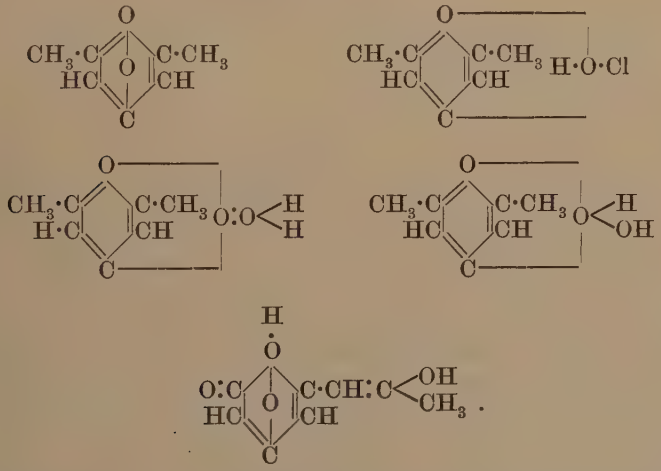


[1] *Annalen*, 1905, **339**, 117.
[2] See also *Ber.*, 1901, **34**, 723 ; 1903, **36**, 3271.
[3] Stolz, *ibid.*, 3279.

The bridging of a five-membered nitrogenous ring is also assumed by M. O. Forster and H. Fierz [1] in the anhydride obtained by dehydration of the hydrazino-compound produced by the reduction of nitrosocamphoryl-ψ-carbamide.



J. N. Collie's [2] assumption of a bridged ring in pyrone derivatives has received considerable attention during the past year, and experimental evidence in favour of his theory has been brought forward by I. F. Homfray.[3] The molecular refraction of pyrone derivatives is abnormal, but the calculated and experimentally determined figures agree fairly closely if the assumption be made that the pyrone compounds contain two quadrivalent oxygen atoms, the atomic refraction for oxygen in this condition being taken as 2·73. Dimethylpyrone, its hydrochloride, its additive compound with alcohol, diacetylacetone and dehydracetic acid are respectively formulated.



Collie's views have, however, been criticised adversely by R. Willstätter and R. Pummerer.[4] These authors formulate the additive product with potassium methoxide with an open chain,[5] since they find

[1] *Trans.*, 1905, **87**, 110, 722.
[2] *Ibid.*, 1904, **85**, 971.
[3] *Ibid.*, 1905, **87**, 1443.
[4] *Ber.*, 1905, **38**, 1461.
[5] *Ibid.*, 1904, **37**, 3740.

that when the potassium is replaced by methyl the resulting compound is the dimethyl ether of bishydroxymethyleneacetone. They consequently now regard the potassium methoxide additive product as resulting from the breaking of the ring and its conversion to the dimethyl ether as simply depending on the direct replacement of potassium by methyl. A similar structure is accorded to the disodium derivative obtained from pyrone. The cyclic formulæ given to these compounds and diacetylacetone by Collie are rejected by Willstätter, in that Collie's formulæ make the two hydroxyls of unequal value, whilst all the evidence is in favour of complete symmetry of structure.

F. Carlo Palazzo [1] alone and jointly with P. Onorato [2] also brings forward evidence for the symmetrical structure of derivatives of pyrone. The ethyl dimethylpyronecarboxylate of Conrad and Guthzeit,[3] like other γ-pyrone compounds, gives no additive product with bromine, but it furnishes dibromo- and tetrabromo-substitution products, the two methyl groups being symmetrically attacked. The authors retain the usual symmetrical pyrone formula for the dimethyldiacetylacetone originally obtained by Thomas and Lefèvre [4] by the action of phosgene on the salts of acetylacetone. Collie agrees in this particular case with such structure on account of the lack of basic properties. But the ketone group of the pyrone ring is, in this case, incapable of furnishing an oxime, so that Collie's assumption of a formula with a bridged ring to explain the impossibility of getting an oxime from dimethylpyrone seems quite unnecessary. Palazzo and Onorato further draw attention to the fact that some years ago F. Feist and H. Belart [5] prepared a dioxime of diacetylacetone,

$$[CH_3\cdot(C{:}NOH)CH_2]_2CO,$$

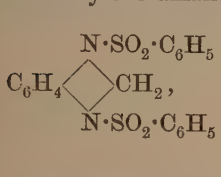
which furnishes an anhydride. This requires two oxygen atoms of similar function in the molecule of diacetylacetone which it will be seen are not accounted for in Collie's formula.

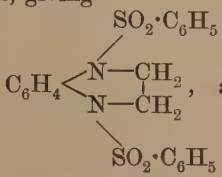
Whether the products obtained by the diazotisation of benzenesulphonylphenylenediamines are cyclic or not, is discussed by G. T. Morgan and F. M. G. Micklethwait.[6] The ortho-compound may well be formulated in such a manner; the para-compound also forms an anhydride which may have a para-bridged ring or be quinonoid in type; the latter explanation is rather suggested by the fact that benzenesulphonyl-*m*-phenylenediamine gives no diazoimide.

The limiting length of a bridged ring has been examined by O. Hinsberg and J. Kessler.[7] Some years back,[8] Hinsberg and

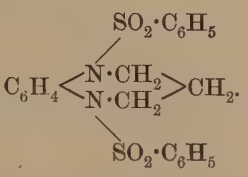
[1] *Gazzetta*, 1905, **35**, [ii], 465. [2] *Ibid.*, 476.
[3] *Ber.*, 1886, **19**, 19; 1887, **20**, 152; *Annalen*, 1891, **261**, 165.
[4] *Bull. Soc. chim.*, 1888, **50**, 193. [5] *Ber.*, 1895, **28**, 1817.
[6] *Trans.*, 1905, **87**, 73.
[7] *Annalen*, 1905, **340**, 110. [8] *Ibid.*, 1895, **287**, 220.

Strupler found that *s*-dibenzenesulphonyl-*o*-phenylenediamine reacts with alkylene dihalides, giving





and



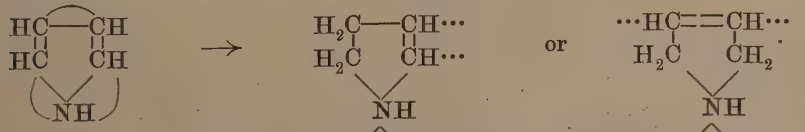
The present authors have carried out similar experiments in the meta- and para-series in order to see what length of chain is necessary, and to get some idea as to the relative distances of the ortho-, meta-, and para-positions. The compounds obtained in the meta- and para-series are, however, bimolecular and of the type

$$C_6H_4{:}[\cdot N(SO_2\cdot C_6H_5)\cdot(CH_2)_n\cdot(C_6H_5\cdot SO_2)N\cdot]_2{:}C_6H_4\,;$$

thus the compound from *s*-dibenzenesulphonyl-*p*-phenylenediamine and trimethylene bromide must be represented as containing an eighteen-membered ring.

Respecting the arrangement of linkings in closed rings, Hinsberg[1] comes to the conclusion that since, as Tichvinsky and Wolochowitz[2] found, the acetylation of dihydrophenazine yields first a monoacetyl derivative—a result he himself confirms—the dihydroazine is probably not symmetrically constituted, and it is more likely that such a constituted dihydro-compound would arise from an *o*-quinonoid form of the azine itself.

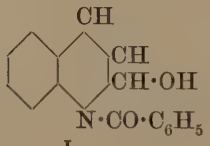
The linkings in the pyrrole molecule are discussed by G. Ciamician,[3] who contrasts the non-basic properties of pyrrole with the salt-forming capability of its dihydro-derivatives. One can apply a symbol similar to Thiele's representation of the benzene molecule to the pyrrole complex, but it necessitates the use of the latent affinity of the nitrogen atom of the ring. If, however, the nucleus be reduced, one immediately has the nitrogen atom occupying the position it has in any other secondary amine and hence capable of forming salts.



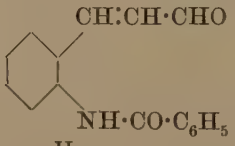
[1] *Ber.*, 1905, **38**, 2800. [2] *Centralbl.*, 1905, [i], 1263; from *Jour. Russ.*, **37**, 8.
[3] *Gazzetta*, 1905, **35**, [ii], 384. See also *Ber.*, 1893, **26**, 1946.

A case of prevention of ring-formation is noticed by Carl Bülow.[1] Ethyl phthalylacetoacetate gives both phenylhydrazone and oxime. The latter may be condensed to an *iso*oxazoline, but the former will not undergo the pyrazoline reaction. Other cases of hindrance of reaction have been observed where both hydrogen atoms of the CH_2 group in ethyl acetoacetate have been replaced by hydrocarbon radicles.[2]

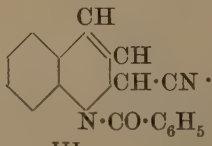
The opening out of closed rings to open-chain compounds has, as usual, engaged some attention. The behaviour of the benzimidazoles to continued alkylation and subsequent treatment with alkali has been studied by Otto Fischer.[3] A very interesting opening out of the quinoline nucleus has been discovered by A. Reissert.[4] Pyridine unites with acetyl chloride [5] and benzoyl choride [6] to form additive products of quaternary ammonium type; these are very easily decomposed by water. Quinoline and benzoyl chloride when mixed develop no heat; nevertheless, Reissert finds that by shaking quinoline and benzoyl chloride with aqueous caustic soda a somewhat bad yield of a compound is obtained which may be formulated as I or II.



I.



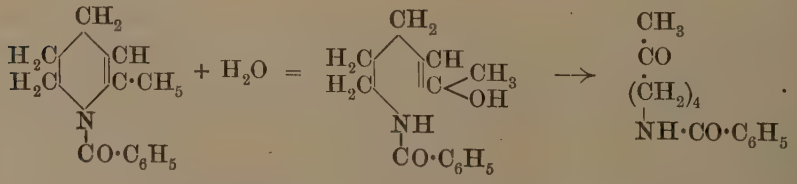
II.



III.

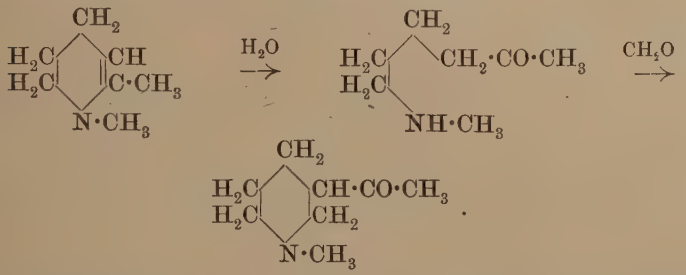
Formula I is favoured by the fact that when the solution of caustic soda is replaced by one of potassium cyanide, a compound of structure III is produced; nevertheless, formula II has to be taken as correct, the substance reacting quite normally with hydroxylamine, aniline, and phenylhydrazine. Reissert has, in addition, examined the following cyclic bases in regard to this reaction: benzthiazole, pyridine, and acridine.

Similarly, when tetrahydro-*a*-picoline is benzoylated, an open-chain compound results.[7]



[1] *Ber.*, 1905, **38**, 1906.
[2] Knorr, *Annalen*, 1887, **238**, 166.
[3] *Ber.*, 1905, **38**, 320.
[4] *Ibid.*, 1603, 3415.
[5] Dennstedt and Zimmermann, *ibid.*, 1886, **19**, 75.
[6] Minunni, *Gazzetta*, 1892, **22**, [ii], 213.
[7] A. Lipp and E. Widnmann, *Ber.*, 1905, **38**, 2276 and 2471.

The fact that tetrahydro-α-picoline reacts with formaldehyde to give a β-substituted piperidine can now be explained, if we suppose that in solution the substance is, by addition of water, in equilibrium with methyl-ε-ketohexylamine. The latter may then react with formaldehyde, the ring closing in a different position.



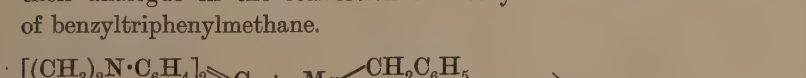
Another case where a new member comes into the ring, studied by Amé Pictet,[1] is involved in the conversion of pyrrole into pyridine derivatives by passage through a red-hot tube. Thus *N*-methylpyrrole gives 2-methylpyrrole and pyridine in succession.

It is of interest to note that the extra carbon atom which comes into the ring forces its way between the α- and β-carbon atoms and not between the α-atom and the nitrogen. This is proved by the conversion of 2-benzylpyrrole to 3-phenylpyridine. In a similar way quinoline is obtained from 2-methylindole, and phenanthridine from methylcarbazole.

Salt Formation and Pseudo-bases.

Quite at the close of 1904, Martin Freund[2] examined the behaviour of quaternary cyclic ammonium salts towards Grignard's reagents. The resulting compounds which are derived from dihydrocyclic substances are but very feebly basic; the reaction reminds one of the production of pseudo-bases.

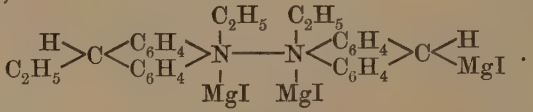
Similar changes occur with *iso*quinoline compounds (cotarnine and hydrastinine salts), and these changes amongst cyclic derivatives find their analogue in the conversion of methyl violet into a derivative of benzyltriphenylmethane.



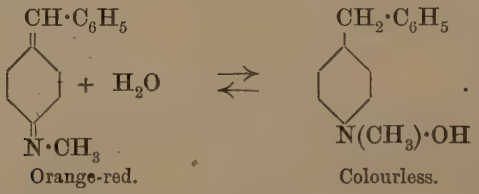
[1] *Ber.*, 1905, **38**, 1946.

[2] *Ibid.*, 1904, **37**, 4666.

Phenylacridine methiodide and magnesium ethyl iodide give α-ethyl-*N*-methylphenyldihydroacridine, which has no basic properties. Acridines themselves (containing tertiary nitrogen) have also been examined in their behaviour to alkyl magnesium halides—A. Senier, P. C. Austin, and R. Clark [1] finding that usually two molecules of the acridine unite with three molecules of the Grignard reagent to form, for example,

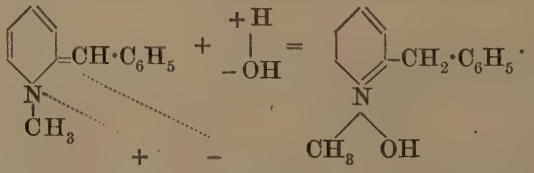


Pseudo-bases have also occupied the attention of H. Decker.[2] When a methylene group is attached to the same carbon atom as that which forms the carbinol group, the elements of water are easily split off; and whilst the salts and true ammonium base may be colourless, the anhydro-bases produced by elimination of water are uniformly coloured.



The first transformation of this type was observed by F. Kehrmann in the quinoxaline series,[3] and subsequently it has been shown that derivatives of pyridine, quinoline, *iso*quinoline, indoline, xanthone, and thioxanthone exhibit the same behaviour.

Employing Thiele's symbol for conjugated partial valencies, Decker uses the following scheme to explain the way in which these are satisfied:

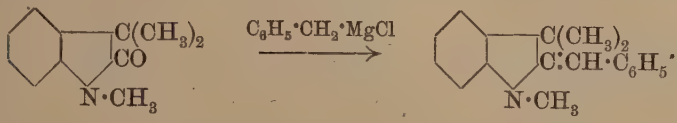


When applied to the *N*-methylacridinium compounds on the one hand and the xanthen and thioxanthen derivatives on the other, the resemblance is most striking.

The conversion of five-membered ring compounds into anhydro-bases

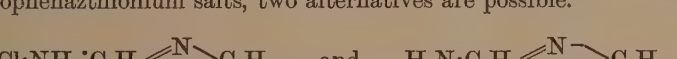
[1] *Trans.*, 1905, **87**, 1469. [2] *Ber.*, 1905, **38**, 2493.
[3] *Ibid.*, 1892, **25**, 1627.

receives a particular application in K. Brunner's production of such a compound by the action of magnesium benzyl chloride on trimethylindolinone.[1]



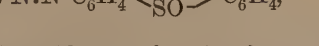
The condition of phenylmethylacridol in solution has been studied by J. J. Dobbie and C. K. Tinkler [2] from a spectroscopic standpoint, the absorption spectra of solutions in ether and chloroform being practically identical with those of dihydroacridine, and quite distinct from those of the original salt. But in alcoholic and aqueous-alcoholic solutions different results are obtained; thus in 50 per cent. methyl alcohol the absorption spectrum closely corresponds with that of 75 per cent. dihydroacridine and 25 per cent. phenylacridine methiodide, addition of water increasing the amount of ammonium compound present.

These results agree well with Hantzsch's idea of pseudo-bases; it has, however, to be kept in mind that the formulation of so many colouring matters with an orthoquinonoid structure involving formation of oxonium salts [3] is not in agreement with Hantzsch's views. Hantzsch has in fact recently pointed out [4] that, for example, the older formulation of Meldola's blue with a paraquinonoid ammonium grouping is in better accord with the properties of the dye than the orthoquinonoid oxonium salt formation proposed by Kehrmann. Taking the simplest aminophenazthionium salts, two alternatives are possible.



Bernthsen. Kehrmann.

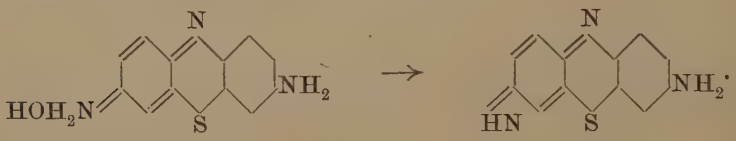
Kehrmann supports his view here, as with the safranines, by the diazotisability of the amino-group. Since, however, the azo-compounds obtained are of the type



Hantzsch argues that the addition of water is a necessary forerunner of the possibility of diazotisation, and the writer would like to draw attention to the fact that in order to diazotise aposafranine it is necessary to work in strongly acid solution.[5] Diazotisability is conditioned by the group $-NH_3A$ rather than the amino-group.

[1] *Ber.*, 1905, **38**, 1359.
[2] *Trans.*, 1905, **87**, 269.
[3] Kehrmann, *Ber.*, 1899, **32**, 2610; 1901, **34**, 1623; *Annalen*, 1902, **322**, 64.
[4] *Ber.*, 1905, **38**, 2143.
[5] Kehrmann, *ibid.*, 1896, **29**, 2316.

Against the view of Kehrmann's, that cyclic oxazine dyes are salts of oxonium type, Hantzsch further brings forward the fact that the chlorides of Lauth's violet, Meldola's blue, and pararosaniline show no more hydrolytic dissociation than does ammonium chloride. Addition of alkali brings about rapid and radical change in the base of Meldola's blue; the hydroxyl base of Lauth's violet seems to have an ephemeral existence, but is probably transformed into an imido-base of the type of Homolka's anhydro-base from magenta,

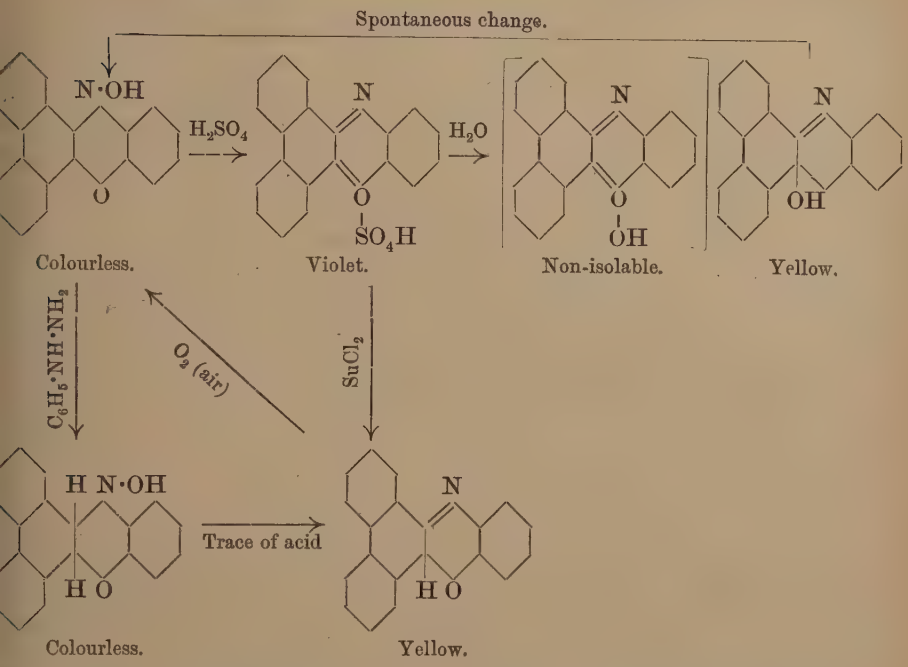


Methylene blue gives a far more stable base, the addition of an equivalent of alkali to the salt not being accompanied by any immediate diminution of electrical conductivity, the gradual decrease which does occur being easily explained by gradual absorption of carbon dioxide and autocatalytic decomposition with formation of methylene azure.

That azoxonium salts in which oxygen plays the part of the salt-forming element are possible, seems incontestable, and Kehrmann [1] has produced a colourless pseudo-phenanthrophenazoxonium hydroxide, $C_{20}H_{13}O_2N$, by the action of *o*-aminophenol on phenanthraquinone.

With acids, violet salts are produced, and the transformations of these substances have been carefully studied. The colourless base is supposed to have hydroxyl attached to nitrogen; a yellow base produced from the salts by the action of water has the hydroxyl group attached to carbon. This yellow form spontaneously isomerises to the colourless variety. The changes may be represented schematically in the following manner:

[1] *Ber.*, 1905, **38**, 2952.



The immediate hydrolysis of the sulphate by water does not alter Kehrmann's views on oxonium salts generally, and when he subsequently synthesises the parent substance of Nile-blue by the action of 4-amino-1 : 2-naphthaquinone on 2 : 5-diaminophenol hydrochloride [1] he does not hesitate to formulate it as

$$H_2N·C_{10}H_5\langle\begin{matrix}N\\OCl\end{matrix}\rangle C_6H_3·NH_2.$$

From the colour of the solution in strong acids and the changes accompanying dilution the existence of tri-acid and di-acid salts must be assumed, and one cannot quite follow the author in supposing that the ammonium groupings are hydrolysed before the oxonium salt groups.

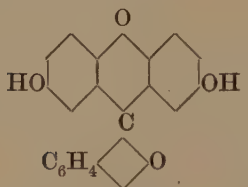
Kehrmann and Gottrau [2] have shown that the supposed oxime of naphthaphenazone of Fischer and Hepp is really an aminonaphthaphenazone, the amino-group having entered the naphthalene nucleus; the oxazone portion is however formulated as a sort of oxonium phenoxide. Fischer and Hepp [3] confirm the correctness of Kehrmann and Gottrau's results, but dispute the oxonium formulation; they contend against Kehrmann's formulation of methylene-blue as a thionium salt, that methylene-azure also forms salts, and pertinently ask if the sulphonyl group is supposed in this case to have a basic character.

[1] *Ber.*, 1905, **38**, 3604. [2] *Ibid.*, 2574. [3] *Ibid.*, 3435.

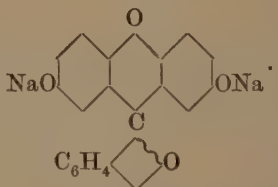
Probably Wedekind and Koch [1] are correct in assigning to santonin nitrate discovered by Andreocci [2] an oxonium constitution, as they have succeeded in preparing a number of double halide salts of santonin.

The formulation of a number of rhodamine salts as of ammonium or oxonium type has engaged the attention of E. Noelting and K. Dziewónski.[3] They find further that the coloured rhodamine salts pass into a colourless form on expulsion of water of crystallisation; for the coloured variety of base they suggest a betaine structure, for the colourless the usual diaminofluorane formulation.

Difficulties in explaining abnormal properties of salts have arisen with regard to the alkaline salts of quinolphthalein.[4] This colourless substance dissolves with strong coloration in alkalis, and R. Meyer and O. Spengler are inclined to see an explanation in the production of "carbonium valency."



Colourless.



Coloured.

Syntheses.

Besides the work which has been done during the past year on the general mechanism of heterocyclic compounds, many new syntheses have been effected and new reactions discovered; an account of these follows, the material being classified according to (*A*) the total number of atoms, and (*B*) the number and nature of atoms other than carbon in the ring.

Pyrrole.

Carl Bülow obtains ethyl *n*-camphyldimethylpyrroledicarboxylate from camphylamine,[5] and ethyl *n*-ureidodimethylpyrroledicarboxylate from semicarbazide and ethyl diacetosuccinate,[6] whilst G. Korschun [7] synthesises ethyl 2 : 3 : 5-trimethylpyrrole-4-carboxylate by the action of ammonia on ethyl α-β-diacetobutyrate.

Pyrrolidine has attracted more attention since the discovery of its 2-carboxylic acid (proline) amongst the products of the hydrolysis of proteids. A new synthesis of pyrrolidine is given by A. Wohl, K.

[1] *Ber.*, 1905, **38**, 421, 429.
[2] *Atti R. Accad. Lincei Roma*, 1896, [v], **5**, ii, 309.
[3] *Ber.*, 1905, **38**, 3516. [4] *Ibid.*, 1903, **36**, 2949; 1905, **38**, 1318.
[5] *Ibid.*, 189. [6] *Ibid.*, 2366. [7] *Ibid.*, 1125.

Schaefer, and A. Thiele,[1] the diethyl acetal of β-chloropropionaldehyde being used as the starting-point. The chlorine atom is replaced by cyanogen, the latter group reduced to $-CH_2 \cdot NH_2$, the benzenesulphonyl derivative of which loses ethyl alcohol with formation of benzenesulphonylethoxypyrrolidine,

$$C_6H_5 \cdot SO_2 \cdot N \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH \cdot O \cdot C_2H_5.$$

The latter compound when reduced by sodium in amyl-alcoholic solution gives pyrrolidine.

A hydroxypyrrolidinecarboxylic acid,

$$NH \cdot CH_2 \cdot CH(OH) \cdot CH_2 \cdot CH \cdot CO_2H,$$

has been synthetically obtained by Hermann Leuchs [2] by the action of ammonia on α-bromo-δ-chloro-γ-hydroxypentoic acid; corresponding to the two asymmetric carbon atoms, two forms have been obtained which much resemble the oxyproline obtained by Fischer on hydrolysing gelatin.[3] For the detection of proline itself, D. Alexandroff [4] recommends the picrates; the racemic form melts at 135—137°, the active at 153—154°.

New pyrrolidine derivatives are described by O. Kühling and Franz Falk,[5] whilst thiopyrrolidone (m. p. 114°) is obtained from pyrrolidone and phosphorus trisulphide.[6]

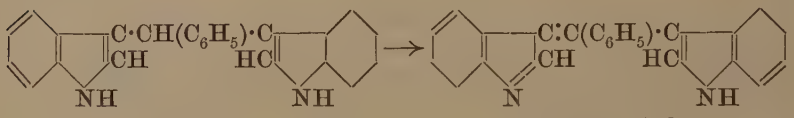
Indole.

G. Mazzara and A. Borgo [7] find that indole is monochlorinated in the 2-position by means of sulphuryl chloride. The substance decomposes with water, giving oxindole. As piperidine compounds are capable of conversion into pyrrolidine derivatives by Merling's method,[8] so may tetrahydroquinoline be transformed into methyldihydroindole. J. von Braun and A. Steindorff [9] find that when benzoyltetrahydroquinoline is treated with phosphorus pentachloride ortho-γ-chloropropylbenzanilide is produced, which, heated under reduced pressure, furnishes *o*-allylbenzanilide. If now hydrogen chloride be added and the benzoyl group removed, ortho-β-chloropropylaniline hydrochloride is produced, the free base readily condensing on warming to the hydrochloride of methyldihydroindole,

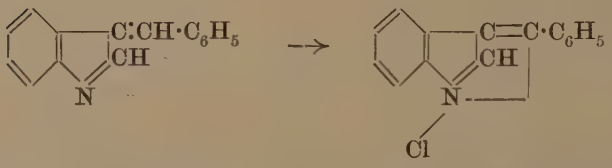
[1] *Ber.*, 1905, **38**, 4154, 4157.
[2] *Ibid.*, 1937.
[3] *Ibid.*, 1902, **35**, 2660.
[4] *Zeit. physiol. Chem.*, 1905, **46**, 17.
[5] *Ber.*, 1905, **38**, 1215.
[6] Tafel and Lavaczek, *ibid.*, 1392.
[7] *Gazzetta*, 1905, **35**, [ii], 320.
[8] *Annalen*, 1891, **264**, 310.
[9] *Ber.*, 1904, **37**, 4723.

A question never previously definitely determined was whether, when an indole is obtained from an α-aminonaphthalene compound, condensation takes place in the ortho-position 2 or in the peri-position 8. Pschorr and Kuhtz[1] have now settled the matter by showing that Schlieper's α-naphthindole[2] and Hinsberg's α-naphthindolesulphonic[3] acid are ortho- and not peri-derivatives.

Martin Freund and Gustav Lebach[4] have examined the colouring matters produced by the action of aldehydes on "methyl-ketol" and other indole compounds. When one molecule of each constituent reacts, a blue dye is produced, but from one molecule of the aldehyde and two molecules of the indole compound the leuco-base of a red dye is formed.



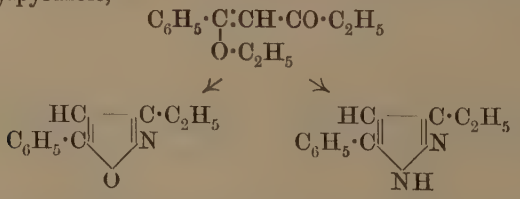
Leuco-base. Colour base (red).



Leuco-base. Coloured salt (blue).

Pyrazoles and Pyrazolones.

The reaction of *o*-ethers of propionylacetophenone with hydroxylamine and hydrazines has engaged the attention of Moureu and Brachin,[5] the first reagent giving 5-phenyl-3-ethyl*iso*oxazole, the latter phenylethylpyrazole,



Fenton finds that phenylhydrazine reacts not only with ethyl ethoxyoxaloacetate to form ethyl phenylhydrazoneketophenylpyrazolone-

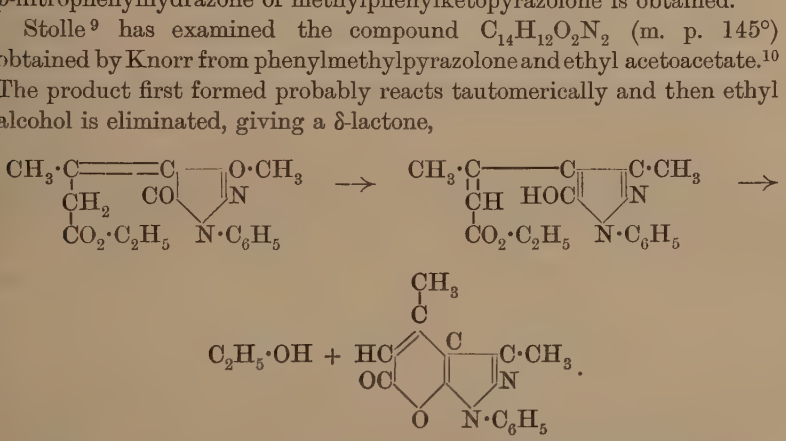
[1] *Ber.*, 1905, **38**, 217. [2] *Annalen*, 1888, **239**, 229.
[3] *Ber.*, 1888, **21**, 110. [4] *Ibid.*, 1905, **38**, 2640.
[5] *Bull. Soc. chim.*, 1905, [iii], **33**, 142.

carboxylate,[1] but that the latter ester may also be obtained from ethyl dihydroxymaleate.[2]

Amongst pyrazolone derivatives, 1-phenyl-5-methyl-3-pyrazolone has been further examined by Michaelis,[3] and 1-phenyl-4-methyl-5-pyrazolone by Michael[4] and Stolz.[5] E. Mohr finds that water is eliminated from phenylmethylpyrazolone at 250°, the carboxyl group of one molecule reacting with a methylene group of a second molecule.[6] 4-Aminoantipyrine gives in succession ethylenediamine and piperazine derivatives with ethylene dibromide and an antipyrine-morpholine with ethylene oxide.[7]

The monohydrazones from ethyl α-β-diketobutyrate have according to A. Wahl[8] a true hydrazone structure, since by acting with *p*-nitrophenylhydrazine on the monophenylhydrazone of the diketobutyric ester, the *p*-nitrophenylhydrazone of methylphenylketopyrazolone is obtained.

Stolle[9] has examined the compound $C_{14}H_{12}O_2N_2$ (m. p. 145°) obtained by Knorr from phenylmethylpyrazolone and ethyl acetoacetate.[10] The product first formed probably reacts tautomerically and then ethyl alcohol is eliminated, giving a δ-lactone,

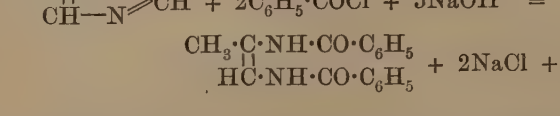


Scholl's[11] product from hydrazine and excess of ethyl acetoacetate is probably constituted similarly and has been examined further by Ludwig Wolff.[12]

Iminazoles.

A very interesting synthesis of methyliminazole is described by Windaus and Knoop,[13] who find that it is produced by the action of an ammoniacal solution of zinc oxide on glucose. As in the case of iminazole itself, the ring is broken by benzoylation,

[1] Wislicenus and Scheidt, *Ber.*, 1891, **24**, 4210.
[2] *Trans.*, 1905, **87**, 810.
[3] *Ber.*, 1905, **38**, 154.
[4] *Ibid.*, 2104.
[5] *Ibid.*, 3273.
[6] *Ibid.*, 2578.
[7] Max Luft, *ibid.*, 4044.
[8] *Bull. Soc. chim.*, 1905, [iii], 33, 490.
[9] *Ber.*, 1905, **38**, 3023.
[10] *Annalen*, 1887, **238**, 182.
[11] *Ibid.*, 1894, **279**, 242.
[12] *Ber.*, 1905, **38**, 3036.
[13] *Ibid.*, 1166.



Pinner finds that phenylglyoxal and ammonia furnish benzoylphenylglyoxaline and 3-hydroxy-1 : 4-diphenylpyrazine.[1]

Triazoles.

The diazotriazolecarboxylic acid ($C_3H_3O_3N_5$), obtained by Thiele and W. Manchot,[2] was regarded as an internal anhydride by its discoverers on account of its stability. Manchot and R. Noll[3] find, however, that a stable derivative is also produced by the diazotisation of ethyl aminotriazolecarboxylate, so that obviously the substance must contain one of the following groups :

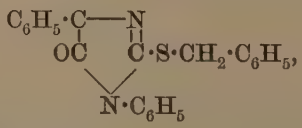
$$—N{=}N{\cdot}OH, \quad —NH{\cdot}NO, \text{ or } {=}N{\cdot}NO.$$

G. Young[4] confirms the constitution of a substance he obtained in 1901 conjointly with Oates[5] from 5-hydroxy-3-phenyl-1-methyl-1 : 2 : 4-triazole by heating with phosphorus pentasulphide as *c*-phenyl-*s*-triazole, since it may also be obtained in the same manner from 5-hydroxy-3-phenyl-1 : 2 : 4-triazole.

In 1900, Wheeler and Dustin[6] obtained a compound containing no sulphur from ethyl diphenylthionsemicarbazidate,

$$C_6H_5{\cdot}NH{\cdot}CO{\cdot}N(C_6H_5){\cdot}NH{\cdot}CS{\cdot}O{\cdot}C_2H_5,$$

and sodium ethoxide, which from analysis might be either a urazole or an oxybiazoline derivative. Wheeler and J. G. Statiropoulos now find[7] that if sodium hydroxide and benzyl chloride be used instead, sulphur is not eliminated, but an undoubted ketodihydrotriazole derivative is formed,

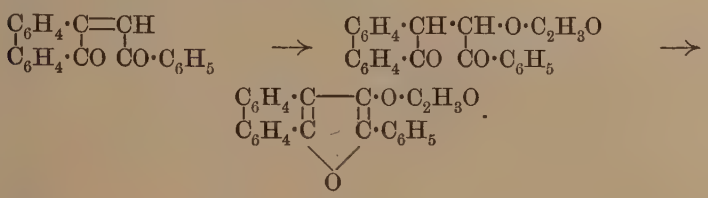


since it can be obtained also by the action of phosgene on diphenylbenzyl-ψ-thiosemicarbazide.

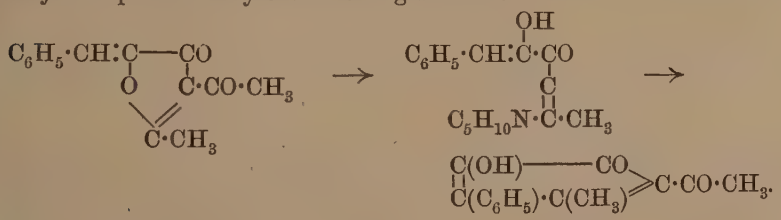
[1] *Ber.*, 1905, **38**, 1531.
[2] *Annalen*, 1898, **303**, 33.
[3] *Annalen*, 1905, **343**, 1.
[4] *Trans.*, 1905, **87**, 625.
[5] *Trans.*, 1901, **79**, 665.
[6] *Ann. Chem. J.*, 1900, **24**, 430.
[7] *Ann. Chem. J.*, 1905, **34**, 117.

Furfuran Group.

F. R. Japp and J. Wood [1] find that phenanthraquinone and acetophenone are condensed to 3-acetoxy-2-phenyl-4 : 5-diphenylenefurfuran by acetic anhydride and sulphuric acid. One has to assume that a carbonyl group of the quinone reacts with the methyl group of the acetophenone, and that the intermediate product thus obtained undergoes the following transformation.



Phenylpropiolyl chloride reacts with the sodium derivative of acetylacetone, giving a substance which S. Ruhemann and R. Merriman find is insoluble in dilute alkaline solutions.[2] It is, therefore, probably cyclic, and if dissolved in piperidine and reprecipitated by hydrochloric acid is found to have been transformed into an isomeride. This change may be represented by the following scheme :



Pyridine Group.

Ahrens [3] gives a process for isolating γ-picoline from the commercial β-picoline, and his pupils have prepared many derivatives ; whilst Formanek [4] finds that pyridine and formaldehyde yield an unstable alkine, $C_5H_4N{\cdot}CH_2{\cdot}OH$.

As usual, a large number of compounds has been obtained by the condensation of methylpyridines with substances containing carbonyl groups,[5] and Königs and von Bentheim [6] show that when aldehydes condense with αα′γ-trimethylpyridine, it is the α-methyl groups which are first attacked. A similar reaction has been studied by R. Franke, who finds that 2 : 5-dimethylpyrazine reacts with one or two molecules of benzaldehyde, giving compounds $C_{13}H_{12}N_2$ and $C_{20}H_{16}N_2$.

[1] *Trans.*, 1905, **87**, 712.
[2] *Ibid.*, 1383.
[3] *Ber.*, 1905, **38**, 155.
[4] *Ibid.*, 944.
[5] *Ibid.*, 2806, 3699, 3704, 3709, 3715.
[6] *Ibid.*, 3907.

W. J. Sell[1] has chlorinated α-picoline; the hexachloropicoline produced is α-trichloromethyl-$\beta\beta'\gamma$-trichloropyridine, since it is successively convertible into trichloropicolinic acid and $\beta\beta'\gamma$-trichloropyridine.

The synthesis of γ-methyl-$\alpha\alpha'$-dihydroxypyridine has been effected by H. Rogerson and J. F. Thorpe,[2] starting with a condensation of the sodium derivative of ethyl cyanoacetate and ethyl acetoacetate. The subsequent transformation can be expressed diagrammatically as follows:

$$CO_2(C_2H_5)\cdot CHNa\cdot CN + CH_3\cdot CO\cdot CH_2\cdot CO_2\cdot C_2H_5 \longrightarrow$$

$$CO_2(C_2H_5)\cdot C(CN)Na\cdot C(OH)(CH_3)\cdot CH_2\cdot CO_2\cdot C_2H_5 \longrightarrow$$

$$CO_2(C_2H_5)\cdot CH(CN)\cdot C(CH_3){:}CH\cdot CO_2\cdot C_2H_5 \xrightarrow{HCl}$$

$$H_2N\cdot CO\cdot CH\cdot(CO_2\cdot C_6H_5)\gg C\cdot CH_3 \longrightarrow$$
$$C_2H_5\cdot O\cdot CO\cdot CH$$

$$NH\lessdot{CO\cdot CH(CO_2\cdot C_2H_5)\atop CO\text{———}CH}\gg C\cdot CH_3 \longrightarrow NH\lessdot{CO\cdot CH_2\atop CO-CH}\gg C\cdot CH_3 \text{ or}$$

$$N\leqslant{C(OH){:}CH_2\atop C(OH)-CH}\gg C\cdot CH_3.$$

The formation of *N*-substituted γ-piperidones has been studied by Charles Mayer;[3] a ketone, $CH_2R\cdot CO\cdot CH_3$, and benzylideneaniline condense to form a substance

$$C_6H_5\cdot N\lessdot{CH(C_6H_5)-CH_2\atop CH(C_6H_5)\cdot CHR}\gg CO.$$

A. Wohl, W. Hertzberg, and M. S. Losanitsch[4] obtain reduced pyridine derivatives from the acetal of the β-chloropropionaldehyde previously mentioned. Two molecules of this substance react with ammonia to give a secondary amine, which undergoes internal condensation on hydrolysis with hydrochloric acid.

$$NH[CH_2\cdot CH_2\cdot CH(O\cdot C_2H_5)_2]_2 \longrightarrow NH[CH_2\cdot CH_2\cdot CHO]_2 \longrightarrow$$

$$NH\lessdot{CH_2\cdot C(CHO)\atop CH_2\text{——}CH_2}\gg CH.$$

With alcohol and hydrochloric acid, not only is the aldehyde group acetalysed, but the elements of hydrogen chloride are added at the double linking, the chlorine atom may be replaced by hydrogen, and a piperidine derivative obtained on reduction with alcohol and sodium.

[1] *Trans.*, 1905, **87**, 799.
[2] *Ibid.*, 1685.
[3] *Bull. Soc. chim.*, 1905, [iii], **33**, 157.
[4] *Ber.*, 1905, **38**, 4161.

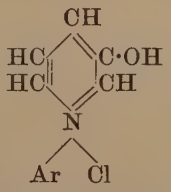
The products of the decomposition of dinitrophenylpyridinium chloride, $C_5H_5N[C_6N_3(NO_2)_2]Cl$, have occupied Zincke's attention;[1] they are open chain compounds of the type

$$NHAr{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}CH{:}NAr,HCl.$$

Their great similarity to the colouring matters obtained from aromatic bases and furfuraldehyde[2] led Zincke to consider these substances as hydroxyl derivatives formed by the opening of the furfuran ring, and to be produced according to the equation

$$C_5H_4O_2 + ArNH_2 + ArNH_2,HCl = H_2O + ArNH{\cdot}CH{:}CH{\cdot}CH{:}C(OH){\cdot}CH{:}NAr,HCl.$$

This view has been confirmed, for, when boiled with acetic acid, one arylamine molecule is eliminated and an arylhydroxypyridinium chloride is produced.[3]



It is remarkable that the same result should have been attained almost simultaneously by W. König[4] and W. Dieckmann and L. Beck.[5]

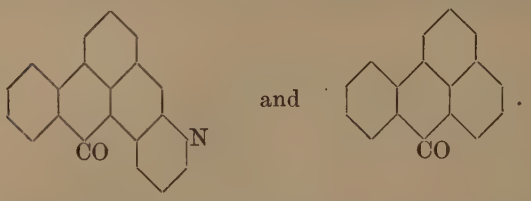
Quinoline.

o-Methylquinoline has been examined by Howitz and Schwenk,[6] new (8 : 8′ and 5 : 5′-dimethyl-8 : 8′) diquinoyls have been prepared by St. von Niementowski and M. Seifert,[7] and the former[8] has prepared γ-hydroxy-α-phenylquinoline-β-carboxylic acid by the condensation of ethyl benzoylacetate with anthranilic acid. Oscar Bally finds that β-aminoanthraquinone does not undergo Skraup's reaction in a normal manner, but reacts with two molecules of glycerol,[9]

$$C_{14}H_9O_2N + 2C_3H_8O_2 = C_{20}H_{11}ON + 7H_2O.$$

The new substance, which he calls benzanthronequinoline, is a derivative of benzanthrone, the substance produced by the interaction of anthraquinone and glycerol; the relationship of the two substances is exhibited by the formulæ

[1] *Annalen*, 1904, **333**, 311; 1905, **339**, 193; **341**, 365.
[2] Stenhouse, *ibid.*, 1870, **156**, 199; H. Schiff, *ibid.*, 1880, **201**, 355; and 1887, **239**, 349.
[3] Zincke and G. Mühlhausen, *Ber.*, 1905, **38**, 3824.
[4] *J. pr. Chem.*, 1905, **72**, 555.
[5] *Ber.*, 1905, **38**, 4122.
[6] *Ibid.*, 1280.
[7] *Ibid.*, 762.
[8] *Ibid.*, 2044.
[9] *Ibid.*, 194.



H. Decker [1] finds that many ortho-substituted quinolines will not combine with methyl iodide owing to steric hindrance, but that the difficulty may be overcome by employing methyl sulphate, a little more than the molecular quantity of which is added to the base, the mixture being heated for 25 to 30 minutes at 100°. Even this process of making quaternary ammonium salts fails with dimethylmesidine, 6-bromodimethylamino-2 : 4-xylene, *N*-methylcarbazole and phenyldinaphthacridine. The nitration of quaternary quinoline compounds follows the same orientation rules as with quinoline itself.[2]

J. Howitz in conjunction with M. Bärlocher [3] and Witte [4] has continued his earlier work on the replacement of bromine by chlorine when *ana*-bromo-*p*-alkyloxy-*N*-methylquinolones are heated with hydrochloric acid. It has now been shown that this labile condition of the halogen atom is not a function of the alkyl or quinolone groups, since several bromohydroxyquinolines react in the same manner.

E. Besthorn and J. Ibele [5] have made further researches on the fluorescent colouring matter, $C_{19}H_{12}ON_2$, obtained from quinaldic acid and acid anhydrides; it may also be obtained from quinaldic chloride and quinoline.

Amongst *iso*quinoline syntheses, Waldemar Findeklee [6] has applied the method of Gabriel and Colman; [7] starting with 4-methylphthalic acid, he has produced eventually 7-methyl*iso*quinoline and 6-methylisatin.

Acridine.

F. Ullmann and R. Fitzenkam employ meta-aminophenols in acridine syntheses,[8] and obtain 2′-methyl-3′-hydroxy-9-phenyl-1 : 2-naphthacridine from 4-amino-*o*-cresol, benzaldehyde, and *β*-naphthol. When tetraaminoditolylphenylmethane reacts with resorcinol, one molecule of *m*-tolylenediamine is eliminated and aminohydroxymethyl*meso*phenylacridine results.

$$C_6H_5\cdot CH[C_6H_2(CH_3)(NH_2)_2]_2 + C_6H_4(OH)_2 + O =$$
$$2H_2O + C_7H_{10}N_2 + HO\cdot C_6H_3\langle{}^{N}_{CPh}\rangle C_6H_2(CH_3)\cdot NH_2.$$

[1] *Ber.*, 1905, **38**, 1144. [2] H. Decker, *ibid.*, 1274. [3] *Ber.*, 1905, **38**, 887.
[4] *Ibid.*, 1260. [5] *Ibid.*, 2127. [6] *Ibid.*, 3542.
[7] *Ibid.*, 1900, **33**, 980. [8] *Ibid.*, 1905, **38**, 3787.

Finally, the replacement of amino-groups by hydroxyl when heated under pressure in sealed tubes has been studied in the case of dihydroxydimethylacridine.[1]

Derivatives of dihydroxyacridone, which results from the condensation of anthranilic acid and phloroglucinol, have been described by W. Baczyński and St. von Niementowski.[2]

K. Friedländer finds that *meso*methylacridine reacts with benzaldehyde to form a base, $C_{13}H_8N{\cdot}CH_2{\cdot}CH(OH){\cdot}C_6H_5$, but if *m*-nitrobenzaldehyde is employed, water is eliminated and a base, $C_{13}H_8N{\cdot}CH{:}CH{\cdot}C_6H_4{\cdot}NO_2$, corresponding to the stilbazoles produced from picolines is obtained.

J. T. Hewitt and J. J. Fox find that the production of para-quinonoid oxygen-free bases from phenylmethylacridol derivatives, when an amino-group occupies the para-position to the carbinol group, holds also in the case of benzoflavine.[3]

Orthodiazines.

F. R. Japp and J. Wood[4] find that the 3 : 4 : 6-triphenyl-1 : 2-diazine obtained previously by Alexander Smith[5] may be obtained from *cis*-dibenzoylstyrene and hydrazine, whilst the latter reacts with dibenzoylstilbene and α-benzoyl-β-trimethacetylstyrene to give tetraphenyldiazine and 3 : 4-diphenyl-6-*tert.*-butyl-1 : 2-diazine respectively.

Phthalazines have been prepared by A. Daube,[6] A. Lieck,[7] and H. Wölbling.[8]

Metadiazines.

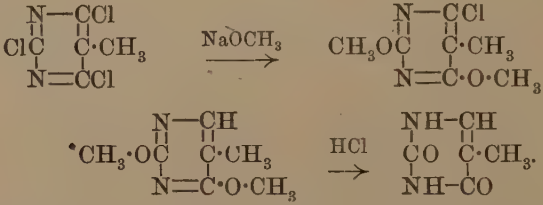
Amongst the metadiazines, new syntheses of uracil and pyrimidine compounds are of foremost interest on account of the near relationship to naturally occurring products. T. Posner[9] has found that when hydroxylamine is added to $\alpha\beta$-unsaturated acids the hydroxylamino-group becomes attached to the β-carbon atom, and does not take up an α-position as previously supposed.[10] Thus, starting with cinnamic acid and hydroxylamine, an aminohydrocinnamic acid was obtained which he has now condensed to phenyldihydrouracil and phenyldihydrothiouracil.

S. Gabriel[11] has re-examined the bromodihydrouracil of E. Fischer and G. Röder.[12] On heating this substance, it loses hydrogen bromide,

[1] See also D.R.-P. 121686.
[2] *Ber.*, 1905, **38**, 3009.
[3] *Trans.*, 1905, **87**, 1058.
[4] *Ibid.*, 707.
[5] *Annalen*, 1896, **289**, 319.
[6] *Ber.*, 1905, **38**, 206.
[7] *Ibid.*, 3918.
[8] *Ibid.*, 3925.
[9] *Ibid.*, 2316.
[10] *Ibid.*, 1903, **36**, 4305.
[11] *Ibid.*, 1905, **38**, 636, 1689.
[12] *Ibid.*, 1901, **34**, 3759.

furnishing uracil from which 2 : 6-dichloropyrimidine and 6-amino-2-chloropyrimidine have been prepared.

Otto Gerngross [1] synthesises 5-methylpyrimidine, starting with carbamide and diethyl *iso*succinate, the hydroxyl groups in the resulting trihydroxymethylpyrimidine being replaced by chlorine, and the latter element replaced by hydrogen. A certain amount of 2-chloro-5-methylpyrimidine is also obtained. Besides numerous other derivatives, the trichloromethylpyrimidine has been employed for a fresh synthesis of thymine,[2] the stages in the process being represented by the following scheme :



Treat B. Johnson and C. O. Johns [3] find that in several cases replacement of halogen by the amino-group in pyrimidine compounds may be effected by heating with aqueous ammonia where Wheeler and Jamieson [4] had failed when using alcoholic ammonia. The same authors [5] have examined 2 : 5-diamino-6-hydroxypyrimidine, which they have obtained by nitration of Wheeler and Jamieson's [6] *iso*cytosine and subsequent reduction ; the diaminohydroxypyrimidines possess considerable interest as possible products of the hydrolysis of the nucleins.[7] Further syntheses of mercaptoaminohydroxypyrimidines are described by T. B. Johnson.[8]

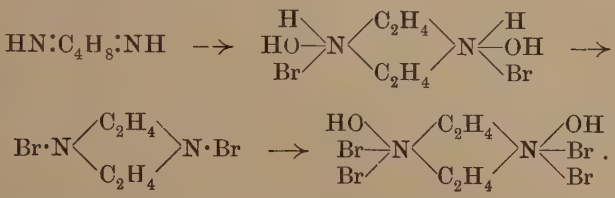
Quinazolines, quinazolones, and diketotetrahydroquinazolines have been examined by S. Gabriel and J. Colman,[9] W. Findeklee,[10] B. Pawlewski,[11] and F. Kunckell.[12]

Paradiazines.

L. Knorr, H. Hörlein, and P. Roth [13] show that Knorr's assumption of the formation of *N*-dimethylpiperazine hydrochloride by the spontaneous polymerisation of methylchloroethylamine is correct, and in a similar way chloroethylpiperidine polymerises to a diquaternary chloride,

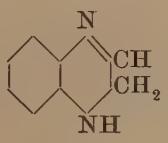
[1] *Ber.*, 1905, **38**, 3394. [2] *Ibid.*, 3408.
[3] *Amer. Chem. J.*, 1905, **34**, 175. [4] *Ibid.*, 1904, **32**, 343.
[5] *Ibid.*, 1905, **34**, 554. [6] *Ibid.*, 1903, **29**, 493.
[7] *Zeit. physiol. Chem.*, 1903, **38**, 176. [8] *Amer. Chem. J.*, 1905, **34**, 191.
[9] *Ber.*, 1905, **38**, 3559. [10] *Ibid.*, 3553.
[11] *Ibid.*, 130. [12] *Ibid.*, 1212. [13] *Ibid.*, 3136.

Piperazine has also attracted the attention of F. D. Chattaway and W. H. Lewis,[1] who find that it reacts with hypobromous acid in the following remarkable manner:

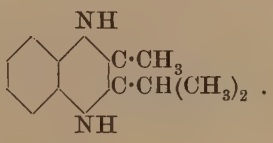


F. R. Japp and J. Knox show that the substance obtained by Japp and Miller[2] from benzil and hydrogen cyanide in alcoholic hydrochloric acid, and subsequently by Minovici[3] by the action of hydrogen chloride on mandelonitrile, is actually 3-keto-2 : 5-diphenyl-3 : 4-dihydro-1 : 4-diazine; on distillation with zinc dust the 2 : 5 diphenyl-1 : 4-diazine of Staedel and Rügheimer[4] and L. Wolff[5] is produced.

Whilst all hitherto known quinoxalines are derivatives of the complex I,



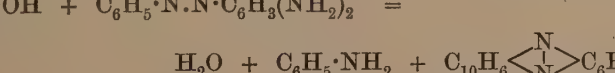
I.



II.

John B. Ekeley and R. J. Wells have obtained a substance to which they ascribe formula II, by the action of *o*-phenylenediamine on mesityl oxide.[6] The presence of two imino-groups seems certain, as the substance gives both dinitroso- and dibenzoyl-derivatives.

F. Ullmann and J. F. Ankersmit describe a new naphthazine synthesis,[7] a typical example of which is furnished by the formation of aminophenonaphthazine from β-naphthol and 2 : 4-diaminoazobenzene,



The product is identical with that obtained by Nietzki and Otto[8] from β-naphthylamine and quinonedichlorodi-imide.

P. Barbier and P. Sisley[9] have revived the question as to the consti-

[1] *Trans.*, 1905, **87**, 951.
[2] *Ibid.*, 1887, **51**, 29.
[3] *Ber.*, 1899, **32**, 2206.
[4] *Ibid.*, 1876, **9**, 563.
[5] *Ibid.*, 1887, **20**, 432.
[6] *Ibid.*, 1905, **38**, 2259.
[7] *Ibid.*, 1811.
[8] *Ibid.*, 1888, **21**, 1599.
[9] *Bull. Soc. chim.*, 1905, [iii], **33**, 995, 1190.

tution of phenosafranine, which was supposed to have been definitely settled in favour of the symmetrical formula :

$$HN{:}C_6H_3\!\leqslant\!\overset{N}{\underset{NPh}{}}\!\!>\!C_6H_3{\cdot}NH_2,\quad HN{:}C_6H_3\!\leqslant\!\overset{N}{\underset{N(C_6H_4{\cdot}NH_2)}{}}\!\!>\!C_6H_4.$$

They have synthesised the unsymmetrical compound by oxidising a mixture of *o-p*-diaminodiphenylamine with aniline and show that it is present in the phenosafranine of commerce.

On examining the electrical conductivity of the salts, it is found that the value soon becomes a maximum with the symmetrical compound, but with the unsymmetrical compound goes on increasing and ultimately exceeds the value in the other case.

F. Sachs and G. Bargellini [1] find that flavinduline condenses with substances containing a reactive methylene group (for example, ethyl acetoacetate, acetylacetone, &c.), oxidation taking place simultaneously.

$$C_{14}H_6\!\leqslant\!\overset{N}{\underset{N(C_6H_5)Br}{}}\!\!>\!C_6H_4 + R{\cdot}CH_2{\cdot}R' + NaOH + O =$$

$$NaBr + 2H_2O + C_{14}H_6\!<\!\overset{\qquad N}{\underset{N(C_6H_5)}{}}\!\!>\!C_6H_3{:}CRR'.$$

Triazines.

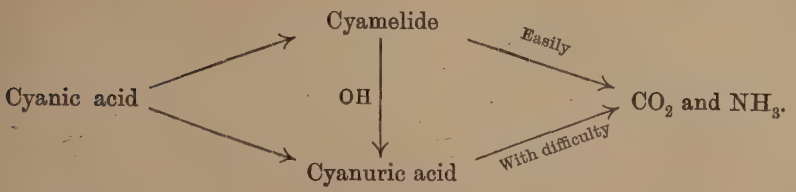
Amongst substances containing three carbon and three nitrogen atoms in the ring, the derivatives of cyanuric acid are especially interesting. A. Hantzsch and H. Bauer [2] have now proved that the cyanilic acid prepared by Liebig by oxidising mellone with nitric acid [3] is identical with cyanuric acid instead of being isomeric. The mixed oxygen and nitrogen ethers of cyanuric acid have been examined, and the series

$$(CN)_3(O{\cdot}CH_3)_3,\quad \left\{\begin{matrix}(CN)_2(O{\cdot}CH_3)_2\\(CO)(N{\cdot}CH_3)\end{matrix}\right\},\quad \left\{\begin{matrix}(CN)(O{\cdot}CH_3)\\(CO)_2(N{\cdot}CH_3)_2\end{matrix}\right\},$$

$$(CO)_3(N{\cdot}CH_3)_3,$$

is now complete. In each case, methyl attached to oxygen is hydrolysed on heating with hydrochloric acid, the linking between nitrogen and methyl not being affected. Hantzsch has also solved the mystery attached to the constitution of cyamelide ; [4] the relationships between this substance, cyanic and cyanuric acids, and the common products of hydrolysis (carbon dioxide and ammonia) is expressed by the following scheme :

[1] *Ber.*, 1905, **38**, 1742.
[2] *Ibid.*, 1005.
[3] *Annalen*, 1834, **10**, 35.
[4] *Ber.*, 1905, **38**, 1013.

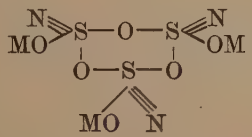


Cyamelide is an extremely weak acid; there is no question of its being a pseudo-acid, and these facts combined with the easy depolymerisation and hydrolysis make the formula

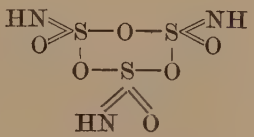
$$\begin{array}{c} HN{:}C{-}O{-}C{:}NH \\ O{\cdot}C(NH){\cdot}O \end{array}$$

extremely probable.

By acting on ammonia with sulphuryl chloride, salts of the *aci*-sulphomelide (I)



I.



II.

have been obtained by Hantzsch and Stuer,[1] but sulphomelide itself (II) could not be isolated.

Syntheses of 1 : 2 : 4-triazine derivatives from semicarbazides and benzil or benzoin have been effected by H. Biltz, Arnd, and Stellbaum.[2]

Tetrazines.

A diphenyldihydrotetrazine (glyoxalosotetrazone) has been obtained by W. Dieckmann and L. Platz[3] by the action of alkalis on chloroglyoxalosazone. The tetrazines (and hydrogenated derivatives) in which the carbon atoms occupy the 1 : 4-position have received more attention. S. Ruhemann and R. Merriman[4] have re-examined the behaviour of tetrazoline towards methyl iodide and shown that the two products which result are

$$NH\!<\!\begin{matrix} CH_2{\cdot}N \\ N{=}CH \end{matrix}\!>\!N\!<\!\begin{matrix} CH_3 \\ I \end{matrix} \quad \text{or} \quad N\!<\!\begin{matrix} N{\cdot}CH_2 \\ CH{=}N \end{matrix}\!>\!N{\cdot}CH_3,HI,$$

and the corresponding periodide, $C_3H_7N_4I_3$.

When an alkaline solution of the methiodide is exposed to the air, a violet coloration is produced, the reaction being compared to the formation of indigotin from indoxyl. If this view is correct, the existence of

[1] *Ber.*, 1905, **38**, 1022.
[2] *Annalen*, 1905, **339**, 243.
[3] *Ber.*, 1905, **38**, 2986.
[4] *Trans.*, 1905, **38**, 1768.

a methylene group in the molecule is necessary, and this receives further support from the fact that tetrazoline condenses with benzaldehyde under the influence of piperidine,

$$C_2H_4N_4 + C_6H_5\cdot CHO = H_2O + C_6H_5\cdot CH{:}C_2H_2N_4,$$

whilst dimethyltetrazoline does not furnish an analogous compound.

D. A. Bowack and A. Lapworth[1] find that bromine reacts with ethyl benzeneazoacetoacetate or diazo-compounds with ethyl acetobromoacetate to yield a bromohydrizino-compound of the structure

$$CBr(:N\cdot NH\cdot C_6H_5)\cdot CO_2\cdot C_2H_5.$$

Under the influence of alkalis, hydrogen chloride is eliminated and two molecules condense to give ethyl diphenyltetrazolinedicarboxylate,

$$\begin{matrix} C(CO_2\cdot C_2H_5){:}N\cdot N\cdot C_6H_5 \\ | \qquad\qquad\quad | \\ N(C_6H_5)\text{——}N{=}C\cdot CO_2\cdot C_2H_5 \end{matrix}\ .$$

By the action of alkalis on the hydrobromide of dihydroxyguanidine,

$$C(:NOH))(NH\cdot OH)(NH_2,HBr),$$

Wieland has obtained the amidoxime of azodicarboxylic acid and the ammonium salt of di-*iso*nitrosotetrahydrotetrazine.[2]

Pyrones and Xanthone Derivatives.

The pyrones themselves have been referred to at some length earlier in this Report, and there is not much to add with reference to the syntheses and characteristic reactions of these compounds.

F. Feist and E. Baum[3] confirm the experience of previous workers as to the difficulty of introducing substituents into the pyrone ring, although pyromeconic acid (3-hydroxypyrone) readily gives 2-halogen substituted derivatives. Maltol (2-methyl-3-hydroxypyrone) and meconic acid (3-hydroxypyrone-2 : 6-dicarboxylic acid) resist bromination, but pyrone may be made to yield 2 : 6-dibromopyrone by warming pyrone with bromine to which a little iodine has been added ; whilst diethyl dibromochelidonate is obtainable from bromine and ethyl acetonedioxalate,

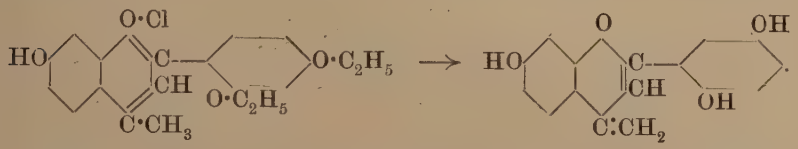
$$\begin{matrix} C_2H_5\cdot CO_2\cdot C{:}O \\ | \\ CH_2\cdot CO\cdot CH_2 \end{matrix}\begin{matrix} \\ | \\ CO\cdot CO_2\cdot C_2H_5 \end{matrix} + 2Br_2 =$$

$$2HBr + H_2O + \begin{matrix} C_2H_5\cdot CO_2\cdot C\text{—}O\text{—}C\cdot CO_2\cdot C_2H_5 \\ \| \qquad\qquad\quad \| \\ BrC\cdot CO\cdot C\cdot Br \end{matrix}.$$

C. Bülow finds that ethyl phthalylacetoacetate gives a coumarin derivative having the formula $C_{18}H_{12}O_6$ when condensed with resorcinol,[4] and conjointly with C. Sautermeister[5] has extended his

[1] *Trans.*, 1905, **87**, 1854. [2] *Ber.*, 1905, **38**, 1443. [3] *Ibid.*, 3562.
[4] *Ibid.*, 474. [5] *Ibid.*, 1904, **37**, 4715.

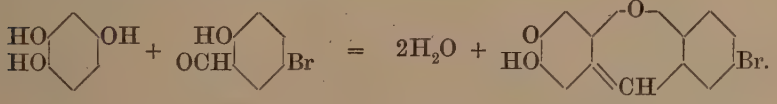
previous work on the synthesis of Nencki and Sieber's resacetein.[1] The synthesis of the last-named compound was effected by condensation of 2 : 4-diethoxybenzoylacetone with resorcinol by means of hydrogen chloride in acetic acid solution, the resulting oxonium salt being next hydrolysed.



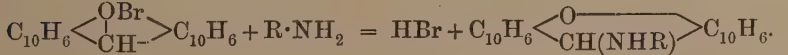
Further compounds of the same class have been prepared by replacing the resorcinol by phloroglucinol and pyrogallol.

The preparation of xanthone derivatives has been rendered easier by the new synthesis of *o*-aryloxybenzoic acids described by F. Ullmann and M. Zlokasoff.[2] These authors find that substances such as sodium phenoxide react readily with sodium *o*-chlorobenzoate under the influence of copper powder, the chlorine being replaced by an aryloxy-group. Aniline in place of the sodium phenoxide gives a diphenylaminecarboxylic acid which readily condenses to acridone as phenylsalicylic acid does to xanthone.

E. Heintschel has studied the synthesis of fluorone derivatives from 1 : 2 : 4-trihydroxyphenol,[3] two molecules of which react normally with one molecule of *m*-nitrobenzaldehyde. Similar reactions take place with 5-nitro- and 5-bromo-salicylaldehydes, although with the last-named compound the reaction also takes a different course, one molecule of each component condensing in the following manner :



The reactions of oxonium salts are in many cases very similar to those of quaternary ammonium compounds, and A. Robin finds that the oxonium bromide corresponding to dinaphthopyranol reacts with aniline much as rosaniline salts react with metallic cyanides.[4]



In the fluorescein group, R. Meyer and H. Pfotenhauer find that phenolphthalein and quinolphthalein give fluorescein on heating with resorcinol ; the reaction is not, however, reversible, since no phenol-

[1] *J. pr. Chem.*, 1881, [ii], **23**, 541.
[2] *Ber.*, 1905, **38**, 2111.
[3] *Ibid.*, 2878.
[4] *Compt. rend.*, 1905, **140**, 1644.

phthalein is produced by heating fluorescein with a large excess of phenol.[1]

M. T. Bogert and R. G. Wright have prepared and examined at length the fluoresceins to be obtained from resorcinol and the nitrophthalic anhydrides; the amino-compounds obtained on reduction are markedly fluorescent.[2]

Only little has to be added with regard to coumarins. H. V. Mitchell has found that salts of benzeneazocoumarinic acid immediately give the corresponding azocoumarins on acidification.[3]

Unclassified Compounds.

The anhydrides of dibasic acids and γ-lactones may call for a few passing remarks, as they contain the same skeletal structure as furfuran. H. Stobbe[4] and his pupils (Leuner, Eckert, and Küllenberg) continue their researches on the "fulgides," derivatives of the anhydride of a still unknown butadiene-$\beta\gamma$-dicarboxylic acid,

$$\begin{matrix} CH_2{:}C\cdot CO \\ | \\ CH_2{:}C\cdot CO \end{matrix}\!\!>\!O.$$

Most of the acids are colourless; the anhydrides are colourless if the hydrogen atoms of the methylene groups are replaced by alkyl radicles, but aromatic radicles as well as the furfuryl group impart a yellow colour which is deeper the greater the number of hydrogen atoms which have been replaced.

A six-membered ring containing both nitrogen and oxygen (lactone) has been produced by A. T. de Mouilpied[1] by condensing ethyl phenylglycinoacetate, $C_6H_5\cdot N(CH_2\cdot CO_2\cdot C_2H_5)_2$, with benzaldehyde or ethyl oxalate. The constitution assigned to the compounds obtained are represented by the formulæ

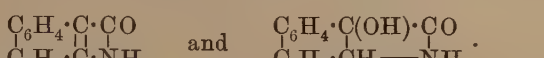
$$CO\!<\!\begin{matrix} O-CH(C_6H_5) \\ CH_2\cdot N(C_6H_5) \end{matrix}\!>\!CH\cdot CO_2\cdot C_2H_5 \qquad \text{and}$$

$$CH\!<\!\begin{matrix} C(OH)-O \\ N(C_6H_5)\cdot C \end{matrix}\!>\!\begin{matrix} C\cdot CO_2\cdot C_2H_5. \\ CO_2\cdot C_2H_5 \end{matrix}$$

The enolic constitution is assigned to the second substance on account of its giving no ketonic reactions, whilst ferric chloride produces a reddish-violet coloration; it is precipitated from its ethereal solution by dry ammonia gas, and also reacts with phenylcarbimide.

[1] *Ber.*, 1905, **38**, 3958. [2] *J. Amer. Chem. Soc.*, 1905, **27**, 1310.
[3] *Trans.*, 1905, **87**, 1229.
[4] *Ber.*, 1905, **38**, 3673, 3682, 3893, 3897, 4075, 4081, 4087.
[5] *Trans.*, 1905, **87**, 435.

F. R. Japp and J. Knox[1] have examined the two compounds, $C_{15}H_9ON$ and $C_{15}H_{11}O_2N$, obtained by Japp and Miller[2] from one of the stereoisomeric cyanohydrins of phenanthraquinone. Both these substances yield salts having the formula $C_{15}H_{10}O_2NNa$, which, however, are not identical, the salt of the compound $C_{15}H_9ON$ regenerating the same substance when the sodium is removed. Consequently the authors formulate the substances as



Phenanthranil. Hydroxydihydrophenanthranil.

These constitutions can be made to account for the reactions of the two substances, but no notice has been taken of the fact that anthranil does not result from the anhydridisation of anthranilic acid and most probably has the constitution

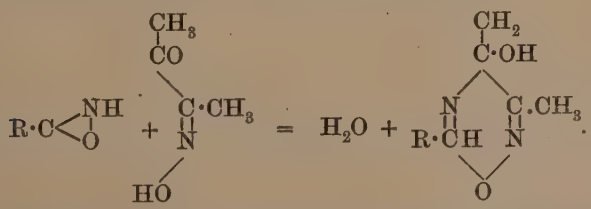
O. Diels and R. van der Leeden have obtained derivatives of a ring containing three carbon, one oxygen, and two nitrogen atoms.[3] Hydrogen chloride acts on the monoxime of diacetyl, giving a salt, $C_6H_{11}O_2N_2Cl$, from which the corresponding base, $C_6H_{10}O_2N_2$, can easily be liberated.

The explanation of the reaction is given by the equations

I. $CH_3{\cdot}CO{\cdot}C(:NOH){\cdot}CH_3 + HCl = CH_3{\cdot}COCl + CH_3{\cdot}CH{:}NOH.$

II. $CH_3{\cdot}CO{\cdot}C(:NOH){\cdot}CH_3 + CH_3{\cdot}CH{:}NOH + HCl =$
$H_2O + C_6H_4O_2N_2Cl,$

and confirmation has been afforded by the condensation of diacetylmonoxime and acetyldioxime to the same compound, whilst benzaldoxime furnishes a corresponding substance, $C_{11}H_{12}O_2N_2$. The condensation probably takes the course represented by the equation



Walter Peters[4] has examined Camp's trimethylenetrisulphone[5] in order to see if it is a pseudo-acid; a comparison of the degree of

[1] *Trans.*, 1905, **87**, 681.
[2] *Ibid.*, 1887, **51**, 29.
[3] *Ber.*, 1905, **38**, 3357.
[4] *Ibid.*, 2565.
[5] *Ibid.*, 1892, **25**, 234.

hydrolysis of its salts with the electric conductivity of the sulphone has been impossible, however, owing to the insolubility of the latter substance.

Compounds of the type of benzophenonesulphone have been prepared by the condensation of diarylsulphone-*o*-carboxylic acids. F. Ullmann and A. Lehner [1] find that diphenylsulphone-*o*-carboxylic acid is readily obtainable by the condensation of the potassium salts of *o*-chlorobenzoic and benzenesulphinic acids, copper powder being used as catalyst.

Some singular derivatives of *o*-benzoic sulphinide (saccharin) have been described by F. D. Chattaway [2] in pursuing his work on nitrogen chlorides:

$$C_6H_4\langle\begin{matrix}CO\\SO_2\end{matrix}\rangle NNa + Cl_2 = C_6H_4\langle\begin{matrix}CO\\SO_2\end{matrix}\rangle N\langle\begin{matrix}Cl_2\\Na\end{matrix} =$$

$$NaCl + C_6H_4\langle\begin{matrix}CO\\SO_2\end{matrix}\rangle NCl.$$

This *N*-chloro-saccharin gives a dipotassium salt,

$$C_6H_4\langle\begin{matrix}CO_2K\\SO(NCl)\cdot OK\end{matrix} \quad \text{or} \quad C_6H_4\langle\begin{matrix}C(NCl)\cdot OK\\SO_3K\end{matrix}.$$

The first of these two formulæ is probably correct, as with excess of potassium hydroxide no *o*-aminobenzoic acid is produced.

Derivatives of a new heterocyclic complex, phenothioxin, are described by F. Mauthner; [3] the dinitro-compound being obtained by the action of picryl chloride on disodium monothiocatechol,

$$C_6H_4\langle\begin{matrix}ONa\\SNa\end{matrix} + \begin{matrix}Cl\\NO_2\end{matrix}\rangle C_6H_2(NO_2)_2 =$$

$$NaCl + NaNO_2 + C_6H_4\langle\begin{matrix}O\\S\end{matrix}\rangle C_6H_2(NO_2)_2.$$

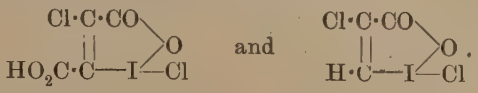
The reaction is based on G. S. Turpin's oxazine synthesis,[4] and the dinitrophenothioxin may be oxidised to a sulphoxide and a sulphone.

S. J. M. Auld and A. Hantzsch [5] have examined the substance obtained by J. E. Reynolds [6] by dissolving mercuric oxide in alkaline aqueous acetone. This compound furnishes salts of the type $C_6H_{10}Hg_3O_3X_2$, and therefore probably contains two hydroxyl groups attached to mercury. Since it is indifferent to hydroxylamine and phenylhydrazine, the authors formulate its production from the first formed dimercuric acetone hydrate in the following manner:

$$2\ \begin{matrix}HC\langle\begin{matrix}Hg\cdot OH\\Hg\cdot OH\end{matrix}\\|\\CH_5\cdot C(OH)_2\end{matrix} = HgO + H_2O + \begin{matrix}Hg\cdot OH \qquad Hg\cdot OH\\|\qquad\qquad\quad|\\HC\text{——}Hg\text{——}CH\\|\qquad\qquad\quad|\\CH_3\cdot C(OH)\cdot O\cdot(HO)\cdot C\cdot CH_3\end{matrix}.$$

[1] *Ber.*, 1905, **38**, 729. [2] *Trans.*, 1905, **87**, 1882. [3] *Ber.*, 1905, **38**, 1411.
[4] *Trans.*, 1891, **59**, 714. [5] *Ber.*, 1905, **38**, 2677. [6] *Zeit. Chem.*, **1871**, 254.

J. Thiele and W. Peter obtain a chloroiodofumaric acid by the action of iodine chloride on acetylenedicarboxylic acid.[1] The iodoso-chloride produced from this contains two, instead of three, chlorine atoms, and hence the acid and the derivative obtained from it by loss of carbon dioxide are formulated respectively as

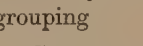


Alkaloids.

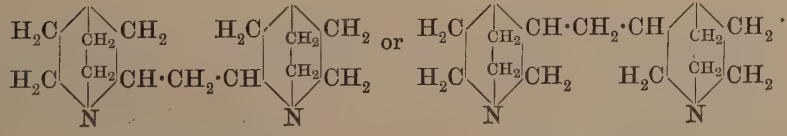
K. Löffler[2] finds that the product obtained by Wertheim[3] by dehydration of conhydrine consists largely of solid, secondary, unsaturated β-coniceine, whilst γ-coniceine occurring in hemlock is, according to J. von Braun and A. Steindorff,[4] α-propyltetrahydropyridine, for, when benzoylated by the Schotten-Baumann method, benzoyl-4-aminobutylpropylketone is produced.[5] The anomalous behaviour of γ-coniceine on alkylation is largely explained by the formula proposed.

According to Amé Pictet,[6] some *N*-methylpyrrolidine is produced when nicotyrine is prepared from nicotine with silver oxide,[7] but the fate of the pyridine nucleus is unknown.

Sparteine has been oxidised by R. Willstätter and W. Marx,[8] who conclude it contains the grouping



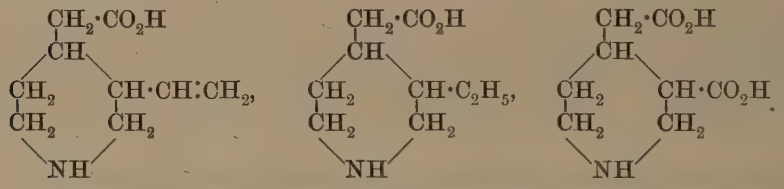
and Ahren's oxysparteine, $C_{15}H_{24}ON_2$, is regarded, not as an aldehyde, but as an oxide of the cineol type. If so, the molecule should contain two tertiary $\equiv$CH groups ; this structure is also required by the formula which Moureu and Valeur have proposed.[9] The latter authors, taking into account that sparteine is a bitertiary amine, and that degradation by Hofmann's method leads to a base, $N{\equiv}C_{15}H_{23}$, combined with an assumed equivalence of the nitrogen atoms and bridged rings in the nuclei, are led to assign (with all reserve) one of the following constitutions to sparteine :



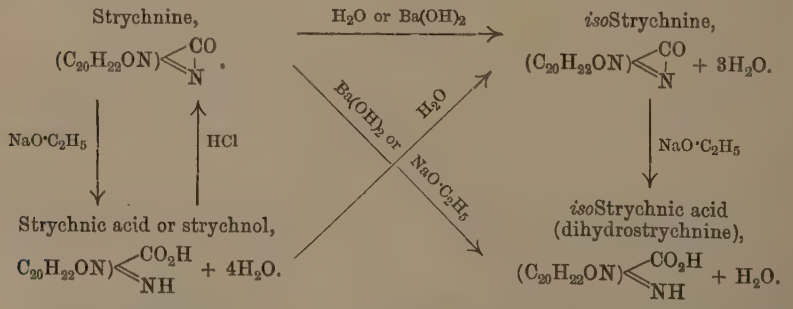
[1] *Ber.*, 1905, **38**, 2842. [2] *Ibid.*, 3326.
[3] *Annalen*, 1856, **100**, 75. [4] *Ber.*, 1905, **38**, 3094.
[5] Compare Lipp and Widnmann, *ibid.*, 2471. [6] *Ber.*, 1905, **38**, 1951.
[7] *Ibid.*, 1894, **27**, 2537. [8] *Ibid.*, 1905, **38**, 1772.
[9] *Bull. Soc. chim.*, [iii], **33**, 1234, 1237, 1244, 1252, 1255, 1266, 1274.

In the quinine group, G. Rohde and G. Schwab[1] have further examined the *iso*nitroso-derivatives of cinchotoxine and quinotoxine,[2] and P. Rabe and K. Ritter[3] find that meroquinene derivatives are readily obtained by application of the Beckmann reaction to *iso*nitroso-methylcinchotoxine, cinchonic acid and the nitrile of methylmeroquinene being produced,

W. Koenig and K. Bernhart[4] have synthesised an inactive β-ethylquinuclidine which so much resembles the active form obtained by reduction of ethyl cincholeuponate as to leave but little doubt that meroquinene, cincholeupone, and cincholeuponic acid are to be represented respectively as



The action of hydrogen peroxide on strychnine furnishes a strychnine-oxide, $C_{21}H_{22}O_3N_2 + 3H_2O$, which A. Pictet and M. Mattisson find belongs to the group of oxamines,[5] whilst A. Bacovescu and A. Pictet[6] have examined Gal and Étard's "hydrates" of strychnine obtained by the action of baryta water.[7] The later work of Loebisch and Schoop[8] and Tafel[9] did not altogether elucidate the reactions taking place, but Bacovescu and Pictet have now established the following genetic relationships:



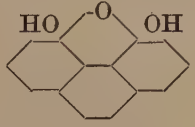
[1] *Ber.*, 1905, **38**, 306.
[2] See also *Ber.*, 1900, **33**, 3217, 3221, 3234.
[3] *Ibid.*, 1905, **38**, 2770.
[4] *Ibid.*, 3049.
[5] *Ibid.*, 2762.
[6] *Ibid.*, 2787.
[7] *Bull. Soc. chim.*, 1879, [ii], **31**, 98.
[8] *Monatsh.*, 1886, **7**, 83.
[9] *Annalen*, 1891, **264**, 33.

New alkaloids of the aconite series have been discovered by W. R. Dunstan and A. E. Andrews.[1] Indaconitine is obtained from "mohri" (*Aconitum chasmanthum*, Stapf), and bikhaconitine from "bikh" (*Aconitum spicatum*). Dunstan and Henry[2] classify the aconite alkaloids, according to whether they yield benzoic or veratric acid on hydrolysis, in the following manner:

Aconitine, $C_{21}H_{27}O_3N(OCO\cdot CH_3)(O\cdot CH_3)_4(OCO\cdot C_6H_5)$.
Japaconitine, $C_{21}H_{29}O_3N(OCO\cdot CH_3)(OCH_3)_4(OCO\cdot C_6H_5)$.
Indaconitine, $C_{21}H_{27}O_2N(OCO\cdot CH_3)(O\cdot CH_3)_4(OCO\cdot C_6H_5)$.
Pseudaconitine, $C_{21}H_{27}O_2N(OCO\cdot CH_3)(O\cdot CH_3)_4(OCO\cdot C_6H_3[O\cdot CH_3]_2)$.
Bikhaconitine, $C_{21}H_{27}ON(OCO\cdot CH_3)(O\cdot CH_3)_4(OCO\cdot C_6H_3[O\cdot CH_3]_2)$.

The alkaloids of opium occupy increasing attention, and the existence of a preformed oxazine (morpholine) ring in morphine, codeine, and thebaine seems to be definitely negatived. L. Knorr[3] arrives at this result partially from the great difference in stability shown by the dihydro-β-naphthyl ether of ethanoldimethylamine (from naphthalanmorpholine),[4] whilst he has also obtained a dihydrocodeinone isomeric with codeine by reduction of codeinone ($C_{18}H_{19}O_3N$, the oxidation product of codeine) with stannous chloride.[5] This dihydrocodeinone is identical with the thebainone, $C_{18}H_{21}O_3N$, produced when thebaine is heated with stannous chloride and hydrochloric acid at 100° (R. Pschorr).[6]

Knorr and Pschorr have jointly examined the decomposition products of thebainone and conclude it contains the non-nitrogenous nucleus

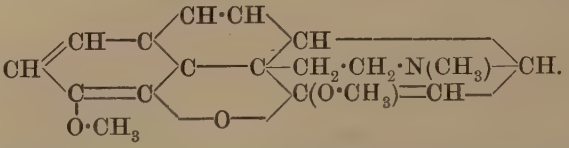


The group $\cdot CH_2\cdot CH_2\cdot N(CH_3)\cdot$ helps to form another ring, and from the proved constitution of papaverine the conclusion is arrived at that these three above-mentioned alkaloids contain the nucleus[7]

M. Freund also comes to the conclusion that thebaine does not contain a morpholine ring,[8] the reaction of thebaine with magnesium

[1] *Trans.*, 1905, **87**, 1620.
[2] *Ibid.*, 1650.
[3] *Ber.*, 1905, **38**, 3143.
[4] *Annalen*, 1899, **307**, 172.
[5] *Ber.*, 1905, **38**, 3171.
[6] *Ibid.*, 3160.
[7] *Ibid.*, 3172.
[8] *Ibid.*, 3234.

phenyl bromide suggesting that a "bridge" oxygen atom has entered into reaction. Freund differs from Pschorr and Knorr in the position he assigns to the ring containing nitrogen, and suggests for thebaine the formula

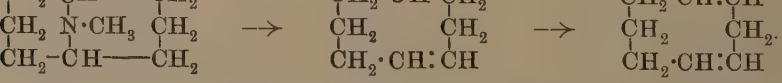


Jowett regards pilocarpine and *iso*pilocarpine as being stereoisomerides[1] and adduces evidence in support of his view; of great importance are the facts that the nitrates of the two bases give identical absorption spectra and that the change from pilocarpine to *iso*pilocarpine is reversible, a small amount of the former base being obtained when the nitrate of the latter is treated with caustic potash. Pinner does not hold with the stereochemical view of the isomerism, for isomerism is only observed so long as the glyoxaline ring remains intact; this portion of the molecule, however, allows of no stereoisomerism.[2]

More recently, Pinner has prepared a new base, metapilocarpine, $C_{11}H_{18}O_3N_2$, by heating the pilocarpine hydrochloride for one to two hours at 225—235°, the product being dissolved in water and then treated with 50 per cent. potassium carbonate. From the oil thus obtained, the metapilocarpine is separated by its insolubility in chloroform.[3]

In connection with work on pilocarpine, Jowett's synthesis of 1 : 4 : 5-trimethylglyoxaline may be mentioned.[4]

Pseudopelletierine is undoubtedly methylgranatonine,[5] and R. Willstätter and H. Veraguth have used methylgranatanine for the production of cyclo-octadiene.[6]



The latter is an easily polymerisable hydrocarbon.

M. Freund and F. Mayer have reduced the methyldihydroberberine of Freund and Beck[7] to a methyltetrahydroberberine standing in a near relationship to corydaline.[8]

O. Fischer and C. Buck are continuing their work on harmaline, $C_{13}H_{14}ON_2$, and describe several new derivatives of apoharmin, $C_8H_8N_2$, and its monocarboxylic acid.[9]

[1] *Trans.*, 1905, **87**, 794. [2] *Ber.*, 1905, **38**, 1510.
[3] *Ibid.*, 2560. [4] *Trans.*, 1905, **87**, 405.
[5] G. Ciamician and P. Silber, *Ber.*, 1892, **25**, 1601; 1893, **26**, 156, 2738; 1894, **27**, 2850; 1896, **29**, 481, 490, 2970. [6] *Ber.*, 1905, **38**, 1975.
[7] *Ibid.*, 1904, **37**, 4673. [8] *Ibid.*, 1905, **38**, 2652. [9] *Ibid.*, 1905, **38**, 329.

Uric Acid Group.

No new syntheses of importance are to be noted in this group. O. Diels and H. Heintzel have obtained hydantoin by the condensation of the sodium derivative of urethane with glycocoll ;[1] Behrend, Meyer, and Rusche have prepared two substances having the formula

$$C_{16}H_{18}O_6N_{12} \text{ and } C_{18}H_{18}O_6N_{12}$$

from glycoluril and formaldehyde ;[2] whilst Bartling shows that a substance obtained by von Vogel on oxidation with nitric acid of a condensation product, $C_{16}H_{26}O_{11}N_{12}S_3$, of *iso*dialuric acid and thiocarbamide is in reality dilituric acid, $C_4H_3O_5N_3$.[3] O. Kühling finds that derivatives of dialuric acid may be obtained through the condensation of alloxan with ketones.[4]

$$C_6H_5\cdot CO\cdot CH_3 + CO\langle\begin{matrix}CO\cdot NH\\CO\cdot NH\end{matrix}\rangle CO \;=\; C_6H_5\cdot CO\cdot CH_2\cdot C(OH)\langle\begin{matrix}CO\cdot NH\\CO\cdot NH\end{matrix}\rangle CO.$$

Some very interesting results have been obtained by W. N. Hartley in studying the spectroscopy of members of the purine group.[5] The simple ureides exhibit no selective absorption, which, however, occurs very markedly when two simple ureides are united by one or more polyvalent atoms. The development of bands in their spectra is produced amongst purine compounds if in the ring a C:O group is converted into an ethylenic linking and a C·OH group adjoining it ; the selective absorption of purine compounds is more marked the greater the number of C:O groups in the ring. Moreover, the formation of salts by addition of alkalis intensifies the selective absorption. The author is in favour of the formula

$$CO\langle\begin{matrix}NH\cdot CO\\NH\cdot C(O\cdot NH_4)\end{matrix}\rangle\!\!=\!\!C\cdot N\!:\!C\langle\begin{matrix}CO\cdot NH\\CO\cdot NH\end{matrix}\rangle CO$$

for murexide.

Natural Colouring Matters.

A new indigo synthesis is that of A. Salmony and H. Simonis, who fuse sodium dianilinomaleate with sodamide and a little caustic potash at 200°.[6]

$$C_6H_5\!-\!\begin{matrix}NH\\HO_2C\end{matrix}\!>\!C\!:\!C\!<\!\begin{matrix}NH\\CO_2H\end{matrix}\!-\!C_6H_5 \;=\; 2H_2O + C_6H_4\langle\begin{matrix}NH\\CO\end{matrix}\rangle C\!:\!C\langle\begin{matrix}NH\\CO\end{matrix}\rangle C_6H_4.$$

The yield is not very good.

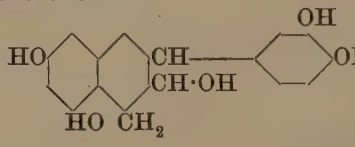
[1] *Ber.*, 1905, **38**, 305.
[2] *Annalen*, 1905, **339**, 1.
[3] *Ibid.*, 37.
[4] *Ber.*, 1905, **38**, 3003.
[5] *Trans.*, 1905, **87**, 1791, 1796.
[6] *Ber.*, 1905, **38**, 2580.

W. P. Bloxam states that "B. A. S. F. indigo pure" contains 91—92 per cent. of indigotin, which he considers is best obtained in a pure condition by sublimation under reduced pressure.[1]

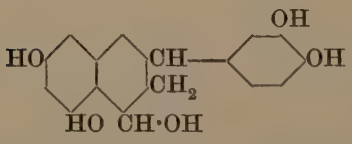
Dimethylenetetroxyindigo has been prepared by P. Herz, starting with nitropiperonal and acetone.[2]

C. Liebermann and G. Häse have examined the condensation products of isatin with pyrrole,[3] on which but little work has been done since their initial discovery by Victor Meyer.[4] Pyrrole blue A has the composition $C_{24}H_{18}O_3N_4$, and pyrrole blue B is $C_{24}H_{18}O_2N_4$.

Amongst the colouring matters of the flavone group, A. G. Perkin's work on catechin and acacatechin must be mentioned.[5] These two substances, although closely related, are quite different. On oxidation of the tetramethyl ethers the same products, veratric acid and phloroglucinol dimethyl ether, are obtained, so that out of the original five hydroxyl groups the positions of four are determined. The isomerism may well be due to the place the fifth hydroxyl group occupies in the molecule, and Perkin suggests the formulæ

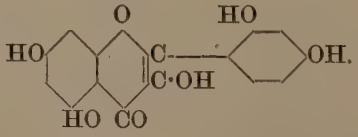


and



as probable.

A. G. Perkin has also examined cyanomaclurin, $C_{15}H_{12}O_6$, a dyestuff of Indian jackwood (*Artocarpus integrifolia*).[6] On fusion with caustic potash, phloroglucinol and β-resorcylic acid are produced, which, taken in conjunction with the constant occurrence of morin with the dyestuff, renders the following structure probable:

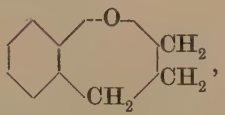


St. von Kostanecki and S. Nitkowski have synthesised fisetin (3 : 3′ : 4′-trihydroxyflavonol), starting with veratraldehyde and the monomethyl ether of resacetophenone;[7] whilst Marie Breger and von

[1] *Trans.*, 1905, **87**, 974.
[2] *Ber.*, 1905, **38**, 2853.
[3] *Ibid.*, 2847.
[4] *Ibid.*, 1883, **16**, 2640; 1884, **17**, 1034.
[5] *Trans.*, 1905, **87**, 398.
[6] *Ibid.*, 1895, **67**, 939; 1905, **87**, 715.
[7] *Ber.*, 1905, **38**, 3587.

Kostanecki describe a second synthesis of apigenin, the initial materials being the dimethyl ether of 2 : 4 : 6-trihydroxyacetophenone and *p*-anisaldehyde.[1] Von Kostanecki and his pupils have also prepared a number of hydroxylated flavones, flavanones, and flavonols, using substituted *o*-hydroxyacetophenones and benzaldehydes as initial products.[2] The methods adopted resemble those described at some length in last year's Report, so that there is no need to enter into details.[3]

It is of interest that chroman,



the parent substance of the group, has been prepared by J. von Braun and A. Steindorff.[4] *o*-Amino-γ-chloropropylbenzene is diazotised and the resulting chloropropylphenol heated with an alkali. Chroman is obtained as a colourless, strongly refractive oil, boiling at 214—215° and having an odour of peppermint.

J. T. Hewitt.

[1] *Ber.*, 1905, **38**, 931.
[2] *Ibid.*, 933, 935, 1507, 2177, 2748.
[3] *Ann. Reports*, 1904, p. 117.
[4] *Ber.*, 1905, **38**, 850.

STEREOCHEMISTRY.

From the point of view of stereochemistry, the past year has been chiefly interesting because of the great simplification which has been effected in the data relating to the configurations of quaternary ammonium salts; a year ago evidence seemed to be rapidly accumulating which indicated that the stereochemical relationships of quinquevalent nitrogen compounds were of far greater complexity than has been found to be the case in connection with carbon compounds. The further investigation of the subject has resulted in a revision of certain of the experimental data, and there now seems nothing to suggest that the stereochemistry of quinquevalent nitrogen and of tetravalent carbon involves considerations differing in kind. But whilst it is now probable that the study of the quaternary ammonium compounds will not immediately lead to any profound modification of those principles which form the basis of stereochemistry, a case has been fairly well established amongst carbon compounds in which the stereochemical relationships cannot be immediately reconciled with our present views concerning maleinoid and fumaroid isomerism. E. Erlenmeyer, jun., and A. Arnold have previously[1] cited data to show that *allo*cinnamic acid is really an externally compensated mixture of two components possessing enantiomorphously related molecular configurations. Erlenmeyer has now[2] extended his previous work and seems to have established that cinnamic and *allo*cinnamic acids are each capable of resolution into two components of enantiomorphously related configurations. The author crystallised *allo*cinnamic acid with brucine, separating about one-half of the acid as a crystalline salt, and then liberated the acid from the latter; the acid thus separated melts at 58—59° and is obtained in enantiomorphously hemihedral crystals, and, from its crystalline form, seems to be identical with the *iso*cinnamic acid which Liebermann extracted from the coca plant. Another and more soluble brucine salt was obtained crystalline from the mother liquors and yielded a cinnamic acid also melting at 58—59°. The two brucine salts melted at 151° and 129° respectively and gave $[\alpha]_D - 24{\cdot}89°$ and $-13{\cdot}98°$ respectively, but the acid separated from

[1] *Ann. Reports*, 1904, p. 132.
[2] *Ber.*, 1905, **38**, 2562, 3496, and 3499.

each was optically inactive. Although the specimens of *allo*cinnamic acid separated from the two brucine salts have the same melting point and are optically inactive, Erlenmeyer presumes them to be distinct substances because of the great apparent differences between the brucine salts from which they are derived. He concludes, further, that he has succeeded in resolving *allo*cinnamic acid into *d*- and *l*- components which should be represented by enantiomorphously related configurations.

On crystallising cinnamic acid itself with brucine, two salts were also obtained. One melted at 135° and gave $[\alpha]_D = 0{\cdot}0°$ in a 1 per cent. solution and $+8{\cdot}82°$ in a 6 per cent. solution; the other salt melted with decomposition at 111—113° and gave $[\alpha]_D - 10{\cdot}84°$ in a 1 per cent. solution. The acid separated from both salts was optically inactive in an 8 per cent. solution and melted at 132—133° or 134°. The examination of the crystals showed, however, that both samples of acids crystallise enantiomorphously and that one set of crystals is enantiomorphously related to the other. It seems thus clear that both cinnamic and *allo*cinnamic acids are externally compensated substances and that each is divisible into two enantiomorphously related components.

In view of the very far-reaching consequences of these results, involving, if they can be substantiated, a revision of our views as to the configurations of maleinoid and fumaroid compounds, it would be interesting to have information on the following points. First, as to whether, on combining the four Erlenmeyer cinnamic acids with optically active bases, four salts, distinguishable in crystalline form, specific and rotatory power, &c., are obtainable; and, second, as to whether the solubilities of the parent cinnamic and *allo*cinnamic acids are respectively different from those of the presumed enantiomorphously related components.

The accomplishment by Marckwald [1] of a true asymmetric synthesis by expelling carbon dioxide from brucine methylethylmalonate by heat —when the valeric acid produced was found to contain an excess of the *l*-isomeride—has led to further work in the same direction. Whilst Marckwald obtained a valeric acid containing only 10 per cent. excess of the *l*-acid, S. Tijmstra, jun.,[2] takes advantage of the fact that the loss of carbon dioxide is the result of a dissociation rather than of a decomposition, and heats the brucine methylethylmalonate in a vacuum at 120° for a short time, instead of heating at 170° under the ordinary pressure. The possibility of isomeric change affecting the result is thus diminished and the valeric acid separated from the product was found to contain 25·8 per cent. excess of *l*-valeric acid.

The Marckwald method for effecting an asymmetric synthesis has been generalised by W. Marckwald and D. M. Paul; [3] they show that advan-

[1] *Ann. Reports*, 1904, p. 133. [2] *Ber.*, 1905, **38**, 2165. [3] *Ibid.*, 810.

tage may be taken of the optical inversion which often occurs on heating optically active acids to convert the externally compensated acid into one optically active component by directing the optical inversion.

Thus, on heating *dl*-mandelic acid with an equivalent quantity of brucine at 150—160° for ten hours and subsequently separating the acid from the salt, it is found to contain an excess of *d*-mandelic acid. This, therefore, forms a distinctly new example of asymmetric synthesis and one to which the objections formerly raised by Cohen and Patterson cannot apply.

McKenzie [1] observes that all commercial samples of fermentation lactic acid are optically active, some being lævo- and others dextro-rotatory. He has accomplished a true asymmetric synthesis of *l*-lactic acid by reducing *l*-menthyl pyruvate with aluminium amalgam—when unequal amounts of *l*-menthyl *d*- and *l*-lactate are formed—and hydrolysing the product with excess of alcoholic potash; the potassium lactate formed contains a preponderance of *l*-lactic acid.

The work of McKenzie [2] has been extended by McKenzie and Thompson [3] in a study of the optical inversion which occurs during the hydrolysis of *l*-menthyl and *l*-bornyl *dl*-phenylethoxyacetates, *dl*-mandelates, *dl*-lactates, and *dl*-ethoxypropionates. On treating the esters with a quantity of alkali insufficient for complete hydrolysis, it is in several cases observed that the initial hydrolysis product contains an excess of the *l*-acid and that on hydrolysing the ester which has survived the initial partial hydrolysis, *l*-acid is also found in preponderating quantity in the resulting acid.

The interpretation of the observed result, that on partially esterifying certain *dl*-acids, such as *dl*-phenylethoxyacetic acid, with a *l*-base hydroxide, such as *l*-menthol, the unesterified acid is lævorotatory, whilst on hydrolysing the ester produced with caustic potash the *l*-acid also preponderates in the regenerated acid, is somewhat as follows. The velocity of formation of the ester, *l*-base, *d*-acid, is greater than that of the ester, *l*-base, *l*-acid; consequently, after the initial esterification stops for lack of sufficient *l*-base, the residual acid contains the *l*-acid in excess. The ester which has been formed contains an excess of the component, *l*-base, *d*-acid, and as the latter, being the most rapidly produced, is in general the most rapidly hydrolysed, it is the first component of the mixed esters to be hydrolysed on contact with the strong caustic alkali. During the initial stage of the hydrolysis, the ester, *l*-base, *d*-acid, is preferentially hydrolysed and, since the caustic potash is still strong, or since the concentration of the hydroxyl ions is still high, the liberated *d*-acid undergoes more or less complete optical inversion. There is now left a preponderance of the ester,

[1] *Trans.*, 1905, **87**, 1373.
[2] *Ann. Reports*, 1904, p. 135.
[3] *Trans.*, 1905, **87**, 1004.

l-base, *l*-acid, and this, being hydrolysed by the remaining weak alkali, in which the concentration of the hydroxyl ions is too small to effect any appreciable optical inversion of the liberated acid, gives rise to a preponderance of the *l*-acid in the final hydrolysis product. In this piece of work, just as in that of Marckwald and Paul above described, a true asymmetric synthesis has been effected.

S. Smiles [1] has attempted an asymmetric synthesis of a thetine. He combined methyl sulphide, methylethyl sulphide, and ethyl sulphide with *l*-menthyl bromoacetate so as to obtain the *l*-menthyl esters of the corresponding thetines; the rotatory powers exhibited by the methylethylthetine ester in various solvents are practically the means of those given by the dimethyl- and diethyl-thetine esters in the same solvents Further, on hydrolysing the esters and so removing the *l*-menthyl group, inactive products were obtained. For these and other reasons, the conclusion is drawn that the two isomeric *l*-menthyl esters of *d*- and *l*-methylethylthetine are produced in equal quantities during the condensation of the sulphide with *l*-menthyl bromoacetate.

Kipping described recently [2] a method for ascertaining whether a particular acid or base is externally compensated, which depends on the following principle. When an externally compensated acid chloride condenses with an externally compensated amine, two externally compensated acid amides are formed; if, however, either the base or amine is not externally compensated but potentially inactive, only one externally compensated acid amide is produced. This method has been applied to a number of cases by E. Mohr.[3]

Marckwald and R. Meth [4] have succeeded in resolving several externally compensated acids and primary bases by taking advantage of the difference between the velocity of formation of an acid amide between a *d*-base and *d*-acid, and between the corresponding *l*-base and *d*-acid. On heating *dl*-mandelic acid with *l*-menthylamine, *d*-mandelic-*l*-menthylamide is formed more rapidly than *l*-mandelic-*l*-menthylamide, the ratio of the velocities of amide formation being $c = 0{\cdot}862$. Similarly, on heating *l*-quinic acid with *dl*-α-phenethylamine, *l*-quinic-*l*-phenethylamide is the more rapidly formed ($c = 0{\cdot}878$); the latter amide, when hydrolysed by heating with hydrochloric acid, yields pure *l*-α-phenethylamine of $[\alpha_D] - 39{\cdot}51°$, together with α-chloroethylbenzene. The latter product is inactive, so that its formation is attended by optical inversion; a number of derivatives of *l*-α-phenethylamine were examined. Objections have been raised by Kipping and Hunter to some of the statements made in this paper.[5]

A very convenient method for the production of resolution of

[1] *Trans.*, 1905, **87**, 450.
[2] *Ann. Reports*, 1904, p. 145.
[3] *J. pr. Chem.*, 1905, **71**, 305.
[4] *Ber.*, 1905, **38**, 801.
[5] *Proc.*, 1905, **21**, 126.

dl-α-phenethylamine has since been given by J. M. Loven.[1] The externally compensated base is crystallised with *l*-malic acid, when a moderately soluble and well-crystallised *d*-phenethylamine hydrogen *l*-malate separates and a very soluble acid salt of the *l*-base remains dissolved; the base is then separated from the mother liquor and crystallised with *d*-tartaric acid, when *l*-phenethylamine *d*-tartrate is easily obtained in a pure state. The properties of the base agree closely with those given by Marckwald and Meth.

The selective action of enzymes on stereoisomeric, but not enantiomorphously, related substances has been long recognised, but with the exception of Fischer's classical isolation of *l*-fructose by the fermentative destruction of the *d*-isomeride contained in synthetic *dl*-fructose, little has been done in the simple chemical treatment of externally compensated substances with enzymes. It has now been shown by E. Fischer and P. Bergell[2] that the pancreatic ferment selectively hydrolyses the optically active components of certain externally compensated dipeptides; synthetic *dl*-leucine-*ld*-alanine is thus partially hydrolysed by pancreatine, yielding *l*-leucine and *d*-alanine. Indications of similar selective hydrolysis were obtained with synthetical externally compensated alanylleucine and leucylleucine. O. Warburg also finds[3] that pancreatine acts on externally compensated leucine ethyl ester with production of *l*-leucine, the *d*-leucine ethyl ester being left unattacked.

H. D. Dakin[4] has continued his investigation of the partial or selective hydrolysis of externally compensated esters by lipase. On treating the methyl, ethyl, *iso*amyl, and benzyl esters of externally compensated mandelic acid with lipase, the *d*-mandelic ester is hydrolysed and the residue contains the *l*-mandelic ester. The hydrolysis of the esters of externally compensated methyl-, ethyl-, *iso*amyl-, and benzyl-mandelic acids by lipase proceeds in a similar manner, the *d*-acid being liberated and the ester of the *l*-acid persisting. Lipase hydrolyses the esters of externally compensated methylphenyl-chloro- and -bromo-acetic acids, and ethylphenyl-chloro- and -bromo-acetic acids in such a way that the *l*-acid is set free and the ester of the *d*-acid is unattacked. The lipase hydrolysis of esters of the externally compensated methylphenylmethoxyacetic acid and ethylphenylethoxyacetic acid proceeds as in the case of the mandelic and alkylmandelic esters.

After administering *dl*-tyrosine, *dl*-leucine, *dl*-aspartic acid, or *dl*-glutaminic acid to rabbits by the mouth, intravenously or subcutaneously, J. Wohlgemuth[5] finds that one component is more or less completely excreted in the urine, whilst the other, the one which is of natural

[1] *J. pr. Chem.*, 1905, **72**, 307. [2] *Ber.*, 1904, **38**, 3103.
[3] *Ibid.*, 1905, **38**, 187.
[4] *J. Physiol.*, 1905, **32**, 199; see also *ibid.*, 1903, **30**, 253.
[5] *Ber.*, 1905, **38**, 2064.

occurrence, is assimilated by the organism. Thus, on administering *dl*-tyrosine, the excreted material consisted of one-half *dl*- and one-half *d*-tyrosine. *dl*-Leucine and aspartic acid appeared in the urine as the *d*-components alone, whilst *dl*-glutaminic acid was excreted as the *l*-component alone.

A. R. Cushny and A. R. Peebles [1] find that *l*-hyoscine and *dl*-hyoscine act similarly on the central nervous system in man and mammals and on the motor terminations in the frog; on the salivary glands and cardio-inhibitory fibres, *l*-hyoscine acts twice as strongly as the externally compensated base. It is thus concluded that *d*- and *l*-hyoscines act equally strongly on the central nervous system, but that whilst *l*-hyoscine acts vigorously on the secretory or cardio-inhibitory nerve fibres, the *d*-isomeride has no such action.

M. O. Forster and H. E. Fierz have prepared [2] a camphoryl-ψ-semicarbazide which has the constitution $C_8H_{14}<\begin{matrix}CH\cdot N(NH_2)\\ |\\ C(OH)-NH\end{matrix}>CO$, and is the first example of an optically active semicarbazide. This substance should prove of service in the resolution of externally compensated aldehydes and ketones, and the more so in that its preparation offers no great difficulties. The semicarbazide gives $[\alpha]_D - 8{\cdot}9°$ in alcoholic solution and reacts with aldehydes and ketones, yielding semicarbazones which in many cases have very high rotatory powers; thus, the camphorylsemi-ψ-carbazones of cinnamaldehyde and *p*-benzoquinone give the values $[M]_D - 2051°$ and $-3310°$ respectively.

Another method for resolving externally compensated aldehydes, ketones, and acids has been shown to be practicable by C. Neuberg and M. Federer; [3] they have prepared phenyl-*d*-amylhydrazine by the action of *d*-amylbromide on sodiophenylhydrazine and have applied it to the resolution of *dl*-arabinose and *dl*-galactose by converting the latter into the corresponding hydrazones. *l*-Arabinosephenyl-*d*-amylhydrazone is less soluble than *d*-arabinosephenyl-*d*-amylhydrazone. Racemic acid was also resolved by converting it into a mixture of *d*- and *l*-tartaric phenyl-*d*-amylhydrazide, the former being the least soluble.

In view of the results obtained by Neuberg and Silbermann, [4] Frankland and Done [5] have again investigated the production and properties of *d*-glyceric acid, preparing the material from externally compensated glyceric acid by four methods based on fermentation with the *Bacillus ethaceticus* and resolution with the aid of brucine. The rotatory powers of the products obtained are in close agreement and show that Frankland and Appleyard's earlier results are correct. [6] Barium *d*-glycerate has the specific rotatory power $[\alpha]_D + 10{\cdot}9°$ in aqueous solution, and

[1] *J. Physiol.*, 1905, **32**, 501.
[2] *Trans.*, 1905, **87**, 826.
[3] *Ber.*, 1905, **38**, 866, 868.
[4] *Ann. Reports*, 1904, p. 137.
[5] *Trans.*, 1905, **87**, 618.
[6] *Ibid.*, 1893, **63**, 299.

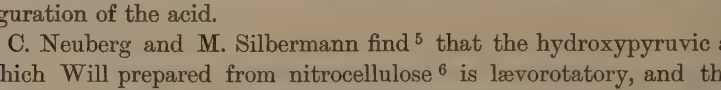
Neuberg and Silbermann's erroneous numbers were due to the use of a faulty instrument.[1]

By subjecting nicotine to very careful purification, F. Ratz has succeeded[2] in increasing its specific rotatory power to a higher value than has been hitherto obtained, namely, $[\alpha]_D - 169{\cdot}54°$ at 20°.

Externally compensated bromopropionic acid has been resolved by E. Fischer and O. Warburg;[3] on crystallising the acid with cinchonine or strychnine, the salt of the *l*-acid separates first, whilst if brucine is used, brucine *d*-bromopropionate is obtained as the least soluble salt.

E. Buchner and R. von der Heide[4] have resolved trimethylene-*trans*-1 : 2-dicarboxylic acid into its optically active components by crystallisation with brucine, quinine, and cinchonidine. The acid has $[M]_D +$ or $-109{\cdot}8°$. *dl*-Trimethylene-1 : 1 : 2-tricarboxylic acid was also resolved by crystallisation with the same bases and gave $[M]_D +$ or $-147{\cdot}5°$. Attempts to resolve synthetical trimethylene-*cis-trans*-1 : 2 : 3-tricarboxylic acid were not successful, as would be expected from the configuration of the acid.

C. Neuberg and M. Silbermann find[5] that the hydroxypyruvic acid which Will prepared from nitrocellulose[6] is lævorotatory, and therefore cannot have the constitution which he assigned to it. It is aldehydoglyceric acid, $CHO{\cdot}CH(OH){\cdot}CO_2H$, and on reduction yields *l*-glyceric acid; the hydroxynitrile formed from it gives *l*-tartaric and mesotartaric acids on hydrolysis, thus:



l-Tartaric acid. *l*-Aldehydoglyceric acid. Mesotartaric acid. *l*-Glyceric acid.

As the configuration of *l*-tartaric acid is as given above, the configurations of the *l*-aldehydoglyceric acid and of *l*-glyceric acid must be also as stated. The conversion of cellulose, a derivative of *d*-glucose, into derivatives of *l*-glyceric acid is similar in kind to the conversion of *d*-glycuronic acid into *l*-xylose and of *d*-galactose into *l*-sorbose.

The labile dihydro-1-naphthoic acid produced by direct reduction of α-naphthoic acid has the constitution $C_6H_4<\begin{matrix}CH(CO_2H){\cdot}CH_2\\ CH=\!=\!=CH\end{matrix}$ or $C_6H_4<\begin{matrix}CH(CO_2H){\cdot}CH\\ CH_2\!-\!-\!-CH\end{matrix}$, and by treatment with caustic soda is converted

[1] *Zeit. physiol. Chem.*, 1905, **44**, 146.
[2] *Monatsh.*, 1905, **26**, 1241.
[3] *Annalen*, 1905, **340**, 168.
[4] *Ber.*, 1905, **38**, 3112.
[5] *Zeit. physiol. Chem.*, 1905, **44**, 134.
[6] *Ber.*, 1891, **24**, 400.

into the stable Δ′-dihydro-1-naphthoic acid, $C_6H_4<\begin{matrix}C(CO_2H):CH\\ CH_2\text{——}CH_2\end{matrix}$. R. H. Pickard and A. Neville[1] have resolved the labile acid by crystallisation with *l*-menthylamine, when the salt *l-B*, *d-A* is obtained as the less soluble isomeride. Δ′-Dihydro-1-naphthoic acid melts at 103°, whilst the externally compensated isomeride melts at 93°; the active acid gave $[\alpha]_D + 212{\cdot}9°$ in chloroform solution and its sodium salt gave the molecular rotatory power $[M]_D + 374{\cdot}5°$ in aqueous solution. The investigation as a time reaction of the conversion of the sodium salt of the active labile acid into that of the potentially optically inactive and stable Δ′-acid when treated with caustic soda showed that the change takes place as a unimolecular reaction; this result, although not decisive, favours the view that the formula first given above correctly represents the constitution of the labile acid.

J. Buraczewski and L. Marchlewski[2] have resolved externally compensated methylmalic acid by crystallisation with strychnine; strychnine *d*-methylmalate is more sparingly soluble than the salt of the *l*-acid.

By crystallising formyl-*dl*-leucine with brucine, E. Fischer and O. Warburg[3] have resolved it into the two optically active components. It is noted that whilst *l*-leucine of natural origin has a slightly bitter taste, the synthetical *dl*- and *d*-leucines have a distinctly sweet taste; *dl*-formylphenylalanine is also resolvable by brucine into its active components.

By heating optically active proteincystine,

$$CH(NH_2)(CO_2H)\cdot CH_2\cdot S\cdot S\cdot CH_2\cdot CH(NH_2)\cdot CO_2H,$$

with hydrochloric acid at 165°, C. Neuberg and P. Mayer[4] have effected its partial optical inversion. The product consists mainly of externally compensated cystine and not of the possible internally compensated isomeride, because it is acted on by *Aspergillus niger* and a *d*-cystine left in the solution.

A comprehensive and valuable compilation, which contains, however, a large quantity of original experimental data, has been presented by P. Walden[5] on the subject of the rotatory power of optically active substances. The author reviews skilfully the work hitherto published on the various factors which influence the numerical values of the rotation constants and illustrates the great effect which the solvent exerts on rotatory power by quoting new data for the rotatory powers of ethyl tartrate, methyl malate, dimethyl *d*-bromosuccinate, methyl *l*-mandelate, and *l*-amyl alcohol in various solvents. He refers to those changes of rotatory power with time which are attributable to tautomerism as

[1] *Trans.*, 1905, **87**, 1763.
[2] *Zeit. physiol. Chem.*, 1905, **44**, 410.
[3] *Ber.*, 1905, **38**, 3997.
Ber., 1905, **38**, 345.
[4] *Zeit. physiol. Chem.*, 1905, **44**, 498.

"tautorotation" and expresses the view that tautomerism and tautorotation occur much more frequently than has hitherto been recognised. From a consideration of new determinations of the rotatory powers of a number of esters in various solvents, the author concludes that the association of the dissolved optically active molecules certainly influences the rotatory power, but that this polymerisation or depolymerisation is not the sole factor determining the change of rotatory power. In a valuable table are collected the rotatory powers of twenty-five substances determined in different solvents, showing that the various solvents used affect the rotatory powers in a certain order; this order is stated below, and to the name of each solvent given is appended, first, the dielectric constant, and, second, the association factor.

Carbon disulphide, 2·64, 1·0; benzene, 2·25, 1·0; chloroform, 4·95, 1·0; ether, 4·52, 1·0; ethyl acetate, 6·74, 1·0; ethyl alcohol, 25·9, 2·7; acetone, 20·7, 1·0 or 1·26; methyl alcohol, 33·2, 3·4; formic acid, 57·0, 3·7; water, 82, 3·6.

The large changes in value of the dielectric constant indicate the influence of the solvent on the rotatory power far better than the smaller variations in the association factor; the former not only gives a true measure of the activity of the solvent in influencing the rotatory power, but also, as is shown by other tables, affords a measure of the chemical activity of the solvent as concerns tautomerising power, dissociating power, &c. One of the most important of Walden's conclusions, namely, that a relation exists between the osmotically determined molecular weight and the rotatory power of an optically active substance dissolved in a particular solvent, has been since criticised adversely by T. S. Patterson,[1] who draws attention to a number of points relating to the rotatory powers and molecular weights of ethyl tartrate and of methyl acetylmalate and malate in various solvents and concludes that no recognisable relation of the kind referred to by Walden exists. It is, for instance, pointed out that although the molecular weight of ethyl tartrate changes rapidly with the concentration in benzene solution, the rotatory power of the ester in this solvent changes but very slightly with the concentration, although the rotatory power of ethyl tartrate differs considerably in different solvents.

T. S. Patterson and F. Taylor have shown[2] that the rotatory power of menthol attains a maximum value of $[M]_D$ −77·94° at 58·3°; at 35·2°, the value is −77·58°, and at 100° it becomes −77·24°. The molecular rotatory powers of *l*-menthyl acetate, *d*-tartrate, and diacetyl-*d*-tartrate change more rapidly than this with temperature, but no points of maximum or minimum rotation were observed. *l*-Menthyl *d*-tartrate gives $[M]_D$ −287·2° at 5·5° and −264·2° at 100°; *l*-menthyl acetate gives $[M]_D$ −157·6° at 13° and 155·6° at 98·1°; *l*-menthyl diacetyl-*d*-

[1] *Ber.*, 1905, **38**, 4090. [2] *Trans.*, 1905, **87**, 33.

tartrate gives $[M]_D$ −258·9° at 14·4° and 227·8° at 99·2°. It is shown that, reasoning by analogy, it is possible to trace the separate effects of the several optically active groups on the molecular rotatory powers of the esters. The same authors [1] have also studied the rotatory powers of *l*-menthol, *l*-menthyl *d*-tartrate, and *l*-menthyl diacetyl-*d*-tartrate when dissolved in ethyl alcohol, benzene, and nitrobenzene, and have obtained data confirming their previous suggestion that the rotatory powers and the molecular solution volumes of an optically active substance in a particular solvent are very closely related factors. Patterson has given a set of values [2] relating to the rotatory power of ethyl *d*-tartrate in chloroform solution and shows that this solvent has a marked effect in depressing the rotatory power of the ester; the changes in rotatory power are in general agreement with the changes in molecular solution volume of the dissolved substance.

P. F. Frankland and N L. Gebhard [3] have prepared the methyl, ethyl, propyl, butyl, heptyl, and octyl dimethoxypropionates by methylating the corresponding esters of *d*-glyceric acid, and have studied their optical activity. The dimethoxypropionates are all lævorotatory, as are also the glyceric esters from which they are derived, but the molecular rotatory powers of the former have much the smaller values. In both series, the molecular rotatory power attains a maximum value in the normal series at the amyl, hexyl, or heptyl ester. The rotatory powers of the dimethoxypropionic esters diminish with a rise of temperature, whilst the reverse occurs with the glycerates and diacetylglycerates.

J. B. Cohen and H. P. Armes [4] have continued the study [5] of the effect of position isomerism on the rotatory power of substituted *l*-menthyl benzoates and confirm the previous conclusion, namely, that the introduction of an ortho-substituting group has the greatest influence, and that of a para-substituting group the least effect, on the rotatory power; the influence of a meta-substituting group is intermediate between that of the other two. In the present investigation, the group introduced was a nitro-group.

A. Haller and M. Desfontaines [6] have prepared a number of esters of β-methyladipic and of γ-methyl-α-alkyladipic acids for comparison with the corresponding esters of 4-methyl-3-*cyclo*pentanecarboxylic acid, obtained from the former by closure of the open chain. It is noticeable that ring formation greatly increases the rotatory power, the rotations observed for the esters of the methylpentamethylenecarboxylic acid being of the order of thirty times as great as those observed for the parent β-methyladipic esters. The introduction of alkyl groups into the

[1] *Trans.*, 1905, **87**, 122. [2] *Ibid.*, 313. [3] *Ibid.*, 864.
[4] *Ibid.*, 1190. [5] *Ann. Reports*, 1904, p. 140.
[6] *Compt. rend.*, 1905, **140**, 1205.

1-position diminishes the rotatory power. J. Minguin contributes [1] observations of the rotatory powers of the esters of amyl alcohol and borneol with succinic, fumaric, and maleic acids which show that the values obtained with the unsaturated acids are higher than those given by the corresponding esters of the unsaturated acids.

Employing the methods previously used, A. Klages and R. Sautter [2] have prepared the following optically active benzene derivatives :

p-$CHMe_2 \cdot C_6H_4 \cdot CH{:}CH \cdot CHMeEt$,	$[\alpha]_D$ +41·89°.
p-$CHMe_2 \cdot C_6H_4 \cdot CH_2 \cdot CH_2 \cdot CHMeEt$,	$[\alpha]_D$ +15·91°.
o-$EtO \cdot C_6H_4 \cdot CH{:}CH \cdot CHMeEt$,	$[\alpha]_D$ +40·97°.
o-$EtO \cdot C_6H_4 \cdot CH_2 \cdot CH_2 \cdot CHMeEt$,	$[\alpha]_D$ +14·99°.

Attempts have been made by D. P. Brace [3] to ascertain whether the rotatory power of a substance is affected by the polarised light ray travelling with or against the earth's rotation. Experiments made on oil of carraway indicated that if any change in rotatory power is thus set up owing to the drag of the ether, it is certainly less than one-five-millionth and probably less than one-ten-millionth part.

In an investigation into the effect produced on the rotatory powers of of *d*-glucose and *d*-fructose by the addition of inorganic salts or electrolytes, E. Rimbach and O. Weber find [4] that the greatest changes of rotatory power are caused by the addition of zirconium salts or of salts like borax, which undergo considerable hydrolytic dissociation; the changes do not proceed instantaneously, and are accompanied by some decomposition of the sugar. Under otherwise constant conditions, the speed with which the rotatory power changes appears to be proportional to the concentration of the hydroxyl ions. Most of the observed changes in rotatory power are to be traced, not to the formation of additive compounds, but to the influence exerted on the degree of breaking down of the sugar molecule by the added electrolyte. This is made clear by the study, as a time reaction, of the effect of caustic soda, sodium carbonate, and triethylamine on the rotatory power of *d*-glucose. The effect produced by the addition of salts and alkalis on the rotatory powers of *d*-glucose, *d*-fructose, and mannitol has also been examined by H. Grossmann.[5] Grossmann and H. Pötter [6] have given the results of an extended investigation of the variations in rotatory power of tartaric acid caused by the addition of molybdates and tungstates. The influence of addition of a number of organic and inorganic compounds to solutions of *d*-glucose on the rotatory power has also been examined by Ina A. Milroy.[7]

[1] *Compt. rend.*, 1905, **140**, 946.
[2] *Ber.*, 1905, **38**, 2312. Compare *Ann. Reports*, 1904, p. 137.
[3] *Phil. Mag.*, 1905, **10**, 383.
[4] *Zeit. physikal. Chem.*, 1905, **51**, 473.
[5] *Ber.*, 1905, **38**, 1711.
[6] *Ibid.*, 3438.
[7] *Zeit. physikal. Chem.*, 1905, **50**, 443.

E. F. Armstrong, in continuing his studies on enzyme action, has obtained important results relating to the synthetical formation of bioses.[1] He regards the process by which α-glucose and β-glucose are converted into the stereoisomeric α- and β-methylglucosides as precisely similar to that by which a monose may be supposed convertible into a biose; and, using the terms α and β to distinguish the glucosides which are hydrolysed by maltase and by emulsin respectively, he indicates that maltose is a glucose-α-glucoside, whilst *iso*maltose is presumably the stereoisomeric glucose-β-glucoside. After allowing fuming hydrochloric acid to act on glucose in the cold, removing the acid, and destroying the residual glucose by fermentation with *Saccharomyces intermedians*, a solution is obtained from which *iso*maltosazone can be separated; on removing the glucose by fermentation with *Saccharomyces Marxianus*, which contains no maltase and is therefore without action on maltose, the solution is found to yield maltosazone. It is thus clear that during the condensation both *iso*maltose and maltose are produced, the former being obtained in much the larger quantity. By the action of maltase extract on glucose, *iso*maltose is produced, and has been separated as *iso*maltosazone. On treating a concentrated glucose solution with 2 per cent. of emulsin at 25° for two months and then destroying the unaltered glucose by the action of *S. Marxianus*, a solution was obtained which yielded maltosazone and which underwent fermentation with a yeast containing maltase. Little, if any, *iso*maltose was produced during this condensation. The condensation of glucose by means of emulsin thus leads to the synthetical formation of maltose, but probably not of *iso*maltose. It is undecided whether the condensation by means of maltase of glucose gives rise to maltose, in addition to *iso*maltose. A convenient method for preparing pure α- and β-methylglucosides in quantity has been given by E. F. Armstrong and S. L. Courtauld.[2]

C. Tanret[3] concurs in the view that the modifications of glucose, lactose, and galactose which he previously regarded as the β-forms, and which exist in the aqueous solution after the rotatory power has become constant, are equilibrium mixtures of the true α- and β-forms. α-Glucose, α-lactose, and α-galactose change into the β-forms when heated at 100°, and on leaving α-glucose at the ordinary temperature the same change occurs very slowly. The α-forms of glucose and galactose are converted into the β-forms when heated in aqueous solution, and the β-form is slowly but completely changed into the α-form by the action of small quantities of water at the ordinary temperature. In the case of the three sugars named, the quantity-ratios in which the α- and β-forms

[1] *Proc. Roy. Soc.*, 1905, **76**, Series *B*, 592.
[2] *Proc. Physiol. Soc.*, 1905, [iv].
[3] *Bull. Soc. chim.*, 1905, [iii], **33**, 337.

are present in the equilibrium mixtures are remarkably similar, namely, 0·368 : 0·632, 0·376 : 0·624 and 0·354 : 0·646 respectively. The β-forms of glucose, galactose, and lactose have the specific rotatory powers $[\alpha]_D + 19°, + 51°$, and + 34·2° respectively in water.[1]

The interconversion of α- and β-methylglucosides in a methyl-alcoholic solution of hydrogen chloride has been studied as a time reaction by C. L. Jungius.[2] The speed of interconversion is approximately proportional to the concentration of the hydrogen chloride, and is greatly diminished by the presence of water; the dynamical study of the reaction does not indicate whether the interconversion is direct as between the α- and β-forms of the glucoside, or whether a third and intermediate acetal form plays a part in the change. The essential cause of the mutarotation of sugar solutions lies in the change $\alpha \rightleftarrows \beta$, and if accompanied by formation of a third hydrated aldehydic form the concentration of the latter is always small. The velocity of interconversion of the methylgalactosides is six to seven times greater than that of the methylglucosides, and at 24° equilibrium is reached between the isomeric glucosides and galactosides when 23 per cent. and 38 per cent. respectively of the β-form is present.

J. C. Irvine and A. Cameron[3] obtained the same tetramethyl-β-methylglucoside by methylating β-methylglucoside and tetramethylglucose[4] with silver oxide and methyl iodide. Tetramethyl-β-methylgalactoside, identical with that previously described, was obtained by similarly methylating β-methylgalactoside.[5] The interconversion of tetramethyl α- and β-methylglucosides has been studied in several solvents, and in each case the presence of small traces of hydrochloric acid is requisite to the interconversion; in methyl-alcoholic solution, the isomeric change of either modification into the other attains equilibrium when 77 per cent. of the α- and 23 per cent. of the β-form are present, practically the same proportion as Jungius found in the equilibrium mixture of the α- and β-methylglucosides.

J. C. Irvine and A. N. Moodie[6] observe that on methylating α-methylmannoside with silver oxide and methyl iodide in methyl-alcoholic solution or tetramethylmannose by heating with methyl alcohol, a crystalline dextrorotatory tetramethyl-α-methylmannoside is the sole product. On treating tetramethylmannose with silver oxide and methyl iodide, a mixture of the above pentamethyl-α-mannoside with an isomeric and lævorotatory liquid tetramethyl-β-methylmannoside is produced. The β-mannoside differs from the α-isomeride in that it is readily hydrolysed by dilute hydrochloric acid or by emulsin.

[1] *Zeit. physikal. Chem.*, 1905, **53**, 692.
[2] *Ibid.*, **52**, 97.
[3] *Trans.*, 1905, **87**, 900.
[4] *Ann. Reports*, 1904, p. 142.
[5] *Ibid.*, p. 143.
[6] *Trans.*, 1905, **87**, 1462.

G. Heikel finds [1] that in anhydrous pyridine solution galactose gives initially the value $[\alpha]_D + 170°$, and that this ultimately changes to $+55{\cdot}6°$. In boiling pyridine, galactose gives $[\alpha]_D + 31°$, and this value gradually changes after cooling to $+59{\cdot}3°$. On acetylating galactose in pyridine solution at 0°, an amorphous pentacetate, presumably the previously unknown α-acetate, is formed; this gives $[\alpha]_D + 71{\cdot}8°$ in benzene solution. On acetylating at higher temperatures in pyridine solution, the known β-pentacetate of $[\alpha]_D + 59{\cdot}2°$ in benzene solution is obtained, together with amorphous products having $[\alpha]_D + 28{\cdot}6°$ to $+60{\cdot}8°$; the formation of the latter substances is taken to indicate the existence of a third or galactose-γ-pentacetate corresponding to the aldehydic form of galactose. Heikel favours the view that the aldohexoses owe their mutarotation to the existence of two interconvertible stereoisomeric lactonic forms, the aldose form being possibly produced as an intermediate stage in the interconversion. R. Behrend [2] regards the case of glucose as probably similar to that of galactose, in that three modifications exist, one having the aldose constitution. He shows that the mutarotation of glucose is not due to hydration by investigating, as a time reaction, the change in rotatory power of α-glucose in pyridine solution at 0°; the change proceeds as a reaction of the first order, whilst if due to hydration it should proceed as one of the second order.

H. E. Armstrong and W. Robertson [3] have prepared and examined a number of hydrazones derived from camphorquinone, some of which have extraordinarily high molecular rotatory powers. Thus, the phenylmethylhydrazone and the phenylbenzylhydrazone of camphorquinone give the values $[M]_D$ 2430° and 2200° respectively. From a consideration of the rotatory powers, the magnetic rotations, and the colours of these and allied substances, the authors are led to suggest modifications in the current mode of representing the constitutions of hydrazones, oximes, and diazo-compounds. They decide that the Hantzsch-Werner hypothesis relating to the isomerism of tervalent nitrogen compounds cannot be upheld; Hantzsch has replied [4] to the arguments brought forward.

The study of the stereochemistry of quaternary ammonium derivatives has been actively pursued during the past year.

Kipping has shown [5] that the isomeric α- and β-salts prepared by the combination of *d*-chloro- and *d*-bromo-camphorsulphonic acids with externally compensated and optically active bases do not, as was previously supposed, owe their formation to stereoisomerism amongst the groups attached to the quinquevalent nitrogen atom. The production of the so-called α- and β-salts is due to the occurrence of isomeric or tautomeric change in the acid used; it is concluded that the ions of

[1] *Annalen*, 1905, **338**, 71. [2] *Ibid.*, 105. [3] *Trans.*, 1905, **87**, 1272.
[4] *Proc.*, 1905, **21**, 288. [5] *Trans.*, 1905, **87**, 628.

the normal and *iso*-forms of the *d*-bromocamphorsulphonic acid have $[M]_D + 280°$ and $+177°$ respectively; the corresponding values for the chloro-acid are $+185·5°$ and $+233°$ respectively. Evidence pointing to the existence of normal and *iso*-forms of ordinary *α*-bromocamphor of a similar nature has been also brought forward by Kipping.[1]

H. O. Jones[2] has shown that the supposed *β*-phenylbenzylallylmethylammonium iodide of Wedekind is really phenylbenzyldimethylammonium iodide. At present, therefore, the only existing evidence indicative of isomerism amongst quaternary ammonium iodides is that afforded by the production of *d*- and *l*-isomerides of the asymmetrically substituted tetralkylammonium salts. The known facts are therefore now all explicable on the assumption previously made that the four alkyl groups attached to a quinquevalent nitrogen atom are situated at the corners of a square, whilst the acidic group lies at the apex of a pyramid erected upon that square, the nitrogen atom being situated within the pyramid.

The optically active asymmetric nitrogen compounds originally prepared by Pope and Peachey[3] have been again examined by A. W. Harvey[4] in order to ascertain whether the specific rotatory powers of the two enantiomorphously related phenylbenzylallylmethylammonium iodides have actually the same numerical values, this point having been left in doubt by Pope and Harvey.[5] The *d*- and *l*-iodides now give the values $[\alpha]_D + 56·2°$ and $-56·8°$, agreeing therefore within the limits of experimental error. Harvey has succeeded in obtaining the four possible salts which can be formed between the *d*- and *l*-bases and *d*- and *l*-camphorsulphonic acids in a state of purity. E. Wedekind has prepared solutions of *d*-phenylbenzylmethylallylammonium hydroxide from the corresponding active iodide by Pope and Peachey's method, and finds that the hydroxide loses none of its optical activity in dilute alcoholic solution—even at 70°; the solution on boiling gradually loses its activity, owing, not to optical inversion, but to decomposition. In aqueous alcohol, the hydroxide has $[M]_D + 192·6°$, a value higher than that observed by Pope and Harvey (166·4°) for the ion of the active base in aqueous solution.

Wedekind has resolved[6] externally compensated *iso*phenylbenzylmethylbutylammonium iodide by Pope and Peachey's method by the use of silver *d*-bromocamphorsulphonate; the salt of the *l*-base is the more sparingly soluble and the iodide gives $[M]_D - 349°$ in alcoholic solution. The active iodide undergoes optical inversion very rapidly in chloroform solution. He has also[7] resolved externally

[1] *Proc.*, 1905, **21**, 125.
[2] *Trans.*, 1905, **87**, 1721.
[3] *Ibid.*, 1899, **75**, 1127.
[4] *Ibid.*, 1905, **87**, 1481.
[5] *Ibid.*, 1901, **79**, 828.
[6] *Ber.*, 1905, **38**, 3933.
[7] *Ibid.*, **37**, 3438.

compensated phenylbenzylmethylpropylammonium iodide by the use of silver *d*-bromocamphorsulphonate; the salt, *l*-base *d*-acid, is the least soluble, and the iodide prepared therefrom shows $[M]_D - 354°$ in alcohol, and very rapidly undergoes optical inversion in chloroform solution.

The following homologous series of optically active quaternary ammonium iodides is now known:

	Phenylbenzylmethylammonium iodides.					
	Ethyl.	Propyl.	*iso*Propyl.	Allyl.	*iso*Butyl.	*iso*Amyl.
$[M]_D$.....	30°	354°	428°	206·4°	349°	478°

In extension of his previous work,[1] H. O. Jones[2] has prepared methyl-*l*-amylaniline and combined it with methyl, allyl, and benzyl iodides. He finds that in the case of phenylmethyl-*l*-amylallylammonium iodide two isomerides are produced; these differ in rotatory power and solubility. The rotatory power of one salt diminishes rapidly in chloroform solution until it finally approximates to the value of that of the other salt, in which no change was observed. On combining benzyl iodide with methyl-*l*-amylaniline, a mixture of two isomeric α- and β-phenylbenzylmethyl-*l*-amylammonium iodides is obtained, and by converting the mixture into the *d*-camphorsulphonate and crystallising, a separation can be effected. β-Phenylbenzylmethyl-*l*-amylammonium *d*-camphorsulphonate and α-phenylbenzylmethyl-*l*-amylammonium *l*-camphorsulphonate were ultimately obtained in a pure state and the corresponding iodides prepared from them. The α-iodide melts at 144—145° and has $[\alpha]_D + 65°$ in chloroform solution, whilst the β-isomeride melts at 131—132° and has $[\alpha]_D - 18·8°$ in chloroform solution; both iodides change in rotatory power in chloroform solution until a final value of $[\alpha]_D + 2·75°$ is attained, owing to dissociation into benzyl iodide and tertiary amine.

Results of a similar kind have been obtained by M. Scholtz[3] in continuation of those previously described.[4] He has prepared stereoisomeric α- and β-quaternary coninium salts in the cases of ethylallylconinium iodide, benzylpropylconinium iodide, and benzylbutylconinium iodide; on heating benzyl-α-ethylconinium iodide at 180—185°, it melts and then gradually solidifies, becoming converted into the β-isomeride melting at 208°. The reverse change could not be effected. The formation of α- and β-isomerides was also observed during the preparation of benzylethylconhydrinium iodide, benzylpropylconhydrinium iodide, and benzyl*iso*amylconhydrinium iodide; the isomerides differ in melting point, solubility and rotatory power, and in physiological activity. The occurrence of similar isomerism was

[1] *Ann. Reports*, 1904, p. 140.
[2] *Trans.*, 1905, **87**, 135.
[3] *Ber.*, 1905, **38**, 595, 1289.
[4] *Ann. Reports*, 1904, p. 146.

not observed during the addition of benzyl iodide to optically active ethyltetrahydroquinaldine.

It is thus shown that when an optically active tertiary amine containing an asymmetric carbon atom combines with an alkyl iodide so as to give a quaternary ammonium salt, which also contains an asymmetric nitrogen atom, two optically active isomerides which are not enantiomorphously related are produced.

Wedekind has ascertained that ethylenedikairolinium hydroxide is not resolved by *d*-camphorsulphonic acid, but on fractional crystallisaation with *d*-bromocamphorsulphonic acid a fraction may be isolated which yields an optically active ethylenekairolinium dibromide, showing $[M]_D + 150°$. Wedekind has thus prepared an optically active compound containing two asymmetric nitrogen atoms, just as Jones and Scholtz have prepared active substances containing one asymmetric carbon and one asymmetric nitrogen atom; these are, therefore, compounds of a similar type to tartaric acid, which owes its optical activity to the presence of two asymmetric carbon atoms.

W. J. Pope.

ANALYTICAL CHEMISTRY.

In reviewing the progress made during the past year in this branch of applied chemistry it will perhaps be best to follow the general plan adopted in my previous report, and to deal with the subjects under the following headings :

1. Inorganic chemistry, including electro-chemical methods.
2. Organic analysis.
3. Analysis of foods and drugs.
4. Toxicological analysis.
5. Apparatus.

It will be obvious that in a review covering such a wide and varied field a proper arrangement of the subject matter is of very great importance, and after much consideration I have been led to adopt the above division as lending itself most readily to methodical treatment, and as being open perhaps to the fewest objections. It is scarcely necessary to point out again that such a sub-division must necessarily be to some extent of an arbitrary character, and in some cases it has of course been found difficult to decide in which of the above categories certain processes should be included. In last year's report, I did not find it necessary to make any special reference to Toxicological Analysis, but in the present one I have thought it advisable to deal with this branch of the subject in a separate section, since, like Food Analysis, it has objects and methods of its own.

Inorganic Analysis.

Owing to the comparatively restricted nature of the qualitative section of this branch of analytical chemistry, useful discoveries are necessarily rare, and there is as a rule but little of importance to record. As an example of the increasing use which is being made of organic compounds both for the detection and estimation of inorganic substances, reference may be made to the suggestion of Alvarez[1] to employ sodium 1-amino-β-naphthol-6-sulphonate as a more delicate

[1] *Compt. rend.*, 1905, **140**, 1186.

test for potassium than even platinic chloride. It is interesting to note that, under suitable conditions, ammonium and magnesium salts are stated not to interfere with this test. Trillat and Turchet [1] have devised a method for the detection of traces of ammonia based on the production of a black coloration or precipitate due to the formation of nitrogen iodide. In order to obtain the best results, iodine chloride in the presence of an alkali is employed as the reagent, and it is stated that, whilst fully as sensitive as Nessler's reagent, it possesses the advantage of being available in the presence of certain substances which either mask or entirely prevent the ordinary Nessler reaction. Blum [2] calls attention to a source of error which may easily occur in applying the ordinary routine procedure for the detection of metals, and which is often overlooked. He points out that ammonium sulphide is prone to undergo oxidation to sulphate and that traces of barium and strontium may in consequence be easily precipitated with the sulphides of groups III and V. The importance of this fact in quantitative separations will be apparent.[3] α-Dimethylglyoxime is suggested by Tschugaeff [4] as a delicate test for nickel, and it is claimed that when properly employed it is capable of detecting one part of that metal in 400,000 parts of water, and of affording certain indications when cobalt is present to the extent of 5000 times that of the nickel. On the other hand, Pozzi-Escot [5] points out that certain derivatives of thiohydantoic acid yield characteristic reactions with cobalt salts and may be usefully employed for the detection of that metal. Benedict [6] finds that potassium periodate constitutes a convenient test for manganese and for cobalt, and shows that by means of this reagent as little as 0·1 per cent. of the latter metal can be detected in nickel salts. Conversely, a manganous salt serves as a delicate test for periodates in the presence of iodates and iodides.

Several new reactions of certain of the rarer elements which appear to be well suited for their detection have been studied during the year and the following seem to be worthy of special notice. Melikoff and Eltschaninoff [7] describe a reaction of columbium which is said to be capable of detecting as little as 0·1 per cent. of that element in tantalum preparations, whilst Alvarez [8] has investigated certain reactions of rhodium and osmium. In the latter case, the test, which depends on the formation of osmium hydriodide, is both characteristic and exceedingly delicate, and, conversely, osmic acid can be used as a sensitive reagent for iodides, even in the presence of bromides and chlorides. The diphenylamine test for nitric acid has been further

[1] *Bull. Soc. chim.*, 1905, **33**, 304.
[2] *Zeit. anal. Chem.*, 1905, **44**, 9.
[3] *Ibid.*, **7**.
[4] *Ber.*, 1905, **38**, 2520.
[5] *Ann. Chim. anal.*, 1905, **10**, 147. *J. Russ. Phys. Chem. Soc.*, 1905, **37**, 99.
[6] *Amer. Chem. J.*, 1905, **34**, 581.
[7] *Compt. rend.*, 1905, **140**, 1254, 1341.

studied by several chemists, and it has been usefully pointed out by Frerichs[1] and by Bay[2] that many oxidising agents other than nitric acid produce the same coloration, and that only under closely defined conditions can the test be regarded as a reliable one for nitrates. A paper by Hinrichs[3] in which an attempt is made to differentiate between nitrates and other oxidising agents is of interest in this connection. In the field of quantitative analytical investigation, perhaps no labour is so valuable and certainly none is more meritorious than that involved in the re-determination or careful revision of important physical constants. As an example of such work, attention may be called to a paper by Worden and Motion[4] giving the densities of solutions of sulphuric, hydrochloric, and oxalic acids and the corresponding percentage strengths. Every possible precaution to ensure accuracy appears to have been taken, and from the tables given the "correction factors" for standard solutions of the above acids can be arrived at with considerable ease, and apparently with great accuracy. Another paper dealing with the preparation of standard hydrochloric acid by a method based on specific gravity determinations has been published by Küster and Münch[5] and may be found useful by chemists engaged in works. The question of the selection of a standard substance for the preparation of the solutions employed in acidimetry is perennial, and has been dealt with during the year by Sörensen and Andersen.[6] The conclusion arrived at by Lunge[7] as the result of an investigation undertaken for the Fifth International Congress of Applied Chemistry, that sodium carbonate is the best of all hitherto studied substances, is dissented from by the above authors, who again put forward claims on behalf of sodium oxalate.[8] It is pointed out incidentally that methyl-orange is not so indifferent to carbonic acid as is usually assumed. North and Blakey,[9] on the other hand, recommend the use of sodium bicarbonate, which they claim to have been able to prepare perfectly free both from moisture and from the normal carbonate. For the estimation of atmospheric carbon dioxide, Horace Brown and Escombe,[10] propose an absorption method based on a novel analytical principle, and which has the practical advantage of rendering unnecessary the measurement of the volume of air employed in the determination. V. Knorre[11] has further studied the application of alkaline persulphates to the separation of lead from other metals, and has shown

[1] *Arch. Pharm.*, 1905, **243**, 80.
[2] *Compt. rend.*, 1905, **140**, 796.
[3] *Bull. Soc. chim.*, 1905, **33**, 1002.
[4] *J. Soc. Chem. Ind.*, 1905, **24**, 178.
[5] *Ber.*, 1905, **38**, 150.
[6] *Zeit. anal. Chem.*, 1905, **44**, 141, 156.
[7] *Zeit. angew. Chem.*, 1904, **17**, 225.
[8] Compare Sebelien, *Chem. Zeit.*, 1905, **29**, 638.
[9] *J. Soc. Chem. Ind.*, 1905, **24**, 395.
[10] *Proc. Roy. Soc.*, 1905, *B*, **76**, 112.
[11] *Zeit. anal. Chem.*, 1905, **44**, 88.

that his previous criticism of Dittrich and Hassel's method was justified, and that the precipitated lead peroxide cannot be completely freed from copper when that metal is present. Dittrich and Reise[1] recommend the use of ammonium persulphate in acid solution as a precipitant of lead, and claim that it is more rapid and convenient than the ordinary precipitation by sulphuric acid with addition of alcohol, and equally accurate. It seems clear, however, in view of the above criticism by v. Knorre, that the method requires further examination, more especially as to the possibility of completely eliminating other metals which may be present. Belton[2] calls attention to the existence of a lead potassium sulphate, and suggests that its formation is sometimes responsible for high results when lead is estimated as sulphate in the presence of potassium salts. Friend[3] has continued his study of the conditions necessary for the correct estimation of hydrogen peroxide in the presence of potassium persulphate, and has also studied[4] those which must be observed if accurate results are to be obtained in the iodometric estimation of permanganate in the presence of persulphate. The estimation of sulphur in pyrites is another perennial problem, and has been studied during the year by H. S. Pattinson[5] and by v. Knorre,[6] the latter of whom finds that the benzidine method suggested by Müller[7] and developed by Raschig is applicable when precautions are taken to neutralise the disturbing effects of the iron, and that accurate results can be obtained. The more general portion of this paper, which deals with the estimation of sulphate in the presence of various metals by means of benzidine, will doubtless be read with interest by analysts. The iodometric estimation of combined sulphurous acid has been made the subject of investigation by Ruff and Jeroch[8] and by Ashley,[9] both of whom point out that the reaction is not so simple as has usually been assumed, and that good results are only to be obtained by a very careful regulation of the conditions. Rupp[10] points out in reply to the adverse criticism of Ruff and Jeroch that those authors had not followed his instructions, and that his method of titration in the presence of sodium bicarbonate does, when properly carried out, give accurate results. For the estimation of mixtures of chlorides, bromides, and iodides, Wentzki[11] has proposed a new method based on the fact that alkali iodides and bromides are converted into chlorides by treatment with mercurous chloride, and that an iodide is converted into bromide by means of mercurous bromide. The results are said to be

[1] *Ber.*, 1905, **38**, 1829.
[2] *Chem. News*, 1905, **91**, 191.
[3] *Trans.*, 1905, **87**, 1367.
[4] *Ibid.*, 738.
[5] *J. Soc. Chem. Ind.*, 1905, **24**, 7.
[6] *Chem. Ind.*, 1905, **28**, 2.
[7] *Ber.*, 1902, **35**, 1587.
[8] *Ibid.*, 1905, **38**, 409.
[9] *Amer. J. Sci.*, 1905, [iv], **19**, 237; **20**, 13.
[10] *Ber.*, 1905, **38**, 1903.
[11] *Zeit. angew. Chem.*, 1905, **18**, 696.

accurate and the method appears to be susceptible of useful application. Tatlock and Thomson [1] describe a process for the determination of small proportions of bromine and chlorine in commercial iodine, which they state they have satisfactorily used for several years, and which appears to possess advantages over the ordinary text-book methods. Jannasch and Jahn [2] have investigated the action of a number of "reducing" agents on chlorates, bromates, and iodates, and find that a hydroxylamine salt is the most convenient reagent for quantitative use. This substance has been previously recommended by Schlötter,[3] and although the paper of Jannasch and Jahn contains much that is not new, it is nevertheless worthy of the attention of analysts. Meisenheimer and Heim [4] describe for the estimation of nitrous and nitric acids, either separately or when present together, a gasometric process based on the evolution of nitric oxide when these acids are decomposed by hydrogen iodide and ferrous chloride respectively. The method appears to be a very useful one, and, judging from the test analyses given, is susceptible of a high degree of accuracy. Simon [5] has made the interesting observation that hydroxylamine can be accurately estimated in its salts by permanganate titration if an excess of sodium oxalate is first added, the mixture behaving as if it were pure hydroxylamine oxalate, and the disturbing effect of the acid radicles being thus eliminated. Another paper by the same author [6] dealing with the action of permanganate on some hydroxylamine salts may be usefully referred to in connection with this subject. In a paper by Reichard,[7] attention is called to the solubility of lithium silicofluoride and to the possibility of employing that salt for the quantitative separation of lithium from sodium and potassium, and a method is discussed for the estimation of the three metals when present together. An accurate and simple method of quantitatively separating tin from antimony is still a desideratum, and the method proposed by Vortmann and Metzl,[8] and depending on the precipitation of the antimony as sulphide from a solution strongly acidified with phosphoric acid, will doubtless be submitted to a thorough examination. Lidholm [9] describes a method for the quantitative separation of silver and lead which appears to yield very good results, and which depends on the reduction of the silver salt to the metallic condition by means of quinol. The gravimetric estimation of bismuth as phosphate has been studied by Staehler and Scharfenberg,[10] who show that under proper conditions this method not only gives accurate results for bismuth alone, but is

[1] *J. Soc. Chem. Ind.*, 1905, **24**, 187.
[2] *Ber.*, 1905, **38**, 1576.
[3] *Zeit. anorg. Chem.*, 1904, **38**, 184.
[4] *Ber.*, 1905, **38**, 3834.
[5] *Compt. rend.*, 1905, **140**, 724.
[6] *Ibid.*, 659.
[7] *Chem. Zeit.*, 1905, **29**, 861.
[8] *Zeit. anal. Chem.*, 1905, **44**, 525.
[9] *Ber.*, 1905, **38**, 566.
[10] *Ibid.*, 3862.

applicable to the separation of that metal from copper, cadmium, mercury, and silver. In connection with this paper, which is deserving of the careful attention of analysts, a communication on the same subject by Salkowski[1] will be read with interest. A most striking example of the way in which synthetical organic substances may be utilised in inorganic analysis is furnished by the observation of Busch[2] that the nitrate of diphenyl *endo*-anilodihydrotriazole is so sparingly soluble in water that the base (known in commerce under the name of "nitron") may be employed for the gravimetric estimation of nitric acid. Several acid radicles interfere with the application of this reagent, but these can, as a rule, be easily eliminated, and as a qualitative test it is interesting to note that a reaction can be obtained in solutions containing as little as one part of the nitrate in 60,000 parts of water. This interesting method has been investigated by Gutbier,[3] who reports very favourably on it, and it is certain to be subjected to rigorous examination by many other chemists.

Baxter and Griffin[4] have again investigated the composition of the ammonium phosphomolybdate formed by carrying out the precipitation under certain defined conditions, and find that a compound of constant composition can be obtained in which the ratio of molybdic acid to triammonium phosphate is always slightly in excess of 12 molecules to 1. Jannasch has continued his able work on the quantitative separation of metals, and, in conjunction with his colleagues, has during 1905 studied more particularly the use of hydroxylamine and hydrazine for this purpose. In collaboration with Rühl, Cohen, and Schilling,[5] he has found that many separations may be easily and accurately effected by ammonia in presence of hydroxylamine, although it is difficult in some cases, as has been pointed out by Friedheim and Hasenclever,[6] to see in what way the new method is superior to those in common use. It should be mentioned, too, that these observers question the possibility of effecting accurately some of the separations referred to below. According to Jannasch and his collaborators, iron may be completely separated by the above reagents from manganese and magnesium; aluminium and chromium from manganese, zinc, nickel, and magnesium; copper from aluminium, chromium, and iron; iron from zinc, and thorium from uranium. In some cases, a single precipitation suffices, but in others a second is necessary, and as a rule the estimation of the metal remaining in solution does not appear to be rendered appreciably more difficult by the presence of the hydroxylamine. This base and hydrazine are also

[1] *Ber.*, 1905, **38**, 3943.
[2] *Ibid.*, 861.
[3] *Zeit. angew. Chem.*, 1905, **18**, 494.
[4] *Amer. Chem. J.*, 1905, **34**, 204.
[5] *J. pr. Chem.*, 1905, [ii], **72**, 1—37.
[6] *Zeit. anal. Chem.*, 1905, **44**, 593.

recommended by Jannasch and von Mayer[1] for the separation of gold from a number of metals, including those of the platinum group. The paper dealing with the latter subject is only a preliminary communication, but the results appear to be of a very useful character, and the further contribution which is promised will be looked forward to with considerable interest by all who are specially concerned with the analytical chemistry of the so-called "noble" metals. Several processes, both gravimetric and volumetric, for the estimation of zinc have been submitted to a critical and comparative study by Nissensen and Kettembeil,[2] and the paper containing the authors' conclusions and results is well worthy of attention. As another instance of useful revision work, attention may be called to a paper by Fernekes and Koch,[3] giving the results of the comparative examination of a number of volumetric processes for the estimation of copper. Kolb and Ahrle[4] call attention to the employment of certain organic acids as precipitants for thorium, and especially recommend *m*-nitrobenzoic acid, a substance which has already been used by Neish[5] for separating thorium from cerium, lanthanum, and didymium. In this connection, attention may be directed to a paper by Grossmann,[6] who effects a separation of the cerite earths from thorium and zirconium by means of sodium sulphite, the last-named metals forming soluble double sulphites on the addition of an excess of the precipitant. In a paper by Béard,[7] the various gravimetric and volumetric processes for the estimation of vanadium are criticised, and a new process based on the precipitation of the vanadium by *α*-nitroso-*β*-naphthol is described. Two interesting and suggestive papers have been published by Glasmann[8] dealing with the volumetric estimation of molybdenum and vanadium by titrating their reduced solutions with permanganate. The chief interest attaching to these communications centres in the fact that vanadium pentoxide is reduced to dioxide by zinc and hydrochloric acid, but to trioxide when magnesium is substituted for the zinc. This fact supplies a striking illustration of the impossibility of regarding "nascent" hydrogen as a definite chemical reagent and one which is independent of the source from which it is derived. There can be no doubt that in all such reduction phenomena the "potential" at which the hydrogen is formed at the metallic surface is an important factor, and as this is to some extent dependent on the nature of the impurities present and the proportions in which they occur, it is more than probable that differences will be noted not only between different metals, but also between various specimens of the

[1] *Ber.*, 1905, **38**, 2129, 2130.
[2] *Chem. Zeit.*, 1905, **29**, 951.
[3] *J. Amer. Chem. Soc.*, 1905, **27**, 1224.
[4] *Zeit. angew. Chem.*, 1905, **18**, 92.
[5] *J. Amer. Chem. Soc.*, 1904, **26**, 780.
[6] *Zeit. anorg. Chem.*, 1905, **44**, 229.
[7] *Ann. Chim. anal.*, 1905, **10**, 41.
[8] *Ber.*, 1905, **38**, 600, 604.

same metal—that is, of course, assuming that these are not of a high degree of purity. That this is at least a partial explanation of the so-called "insensitiveness" of zinc when used in the Marsh-Berzelius flask for the detection of traces of arsenic has been shown by the author of this report, in conjunction with H. D. Law, in a preliminary note,[1] and the study of the reduction of molybdenum and vanadium compounds from this point of view is now being undertaken. For the estimation of the heptamolybdates, Glasmann[2] has described an accurate iodometric method which appears to be applicable also to the analysis of polytungstates. V. Knorre[3] has applied the benzidine method to the estimation of tungsten either in its compounds or in tungsten steel, and finds that good results can be obtained. This appears to be a useful process, and affords another example of the services which organic compounds are capable of rendering to inorganic analytical chemistry. This indeed constitutes one of the most promising fields of research at the present time. Two papers by Rose,[4] dealing with cupellation and parting in gold ore assaying, will be read with interest by all who devote themselves to this branch of analysis. Cantoni and Chautems[5] have based on the volatility of a methyl ester of arsenious acid a method for separating arsenic from antimony which appears to be susceptible of useful application in toxicological investigations. The method is very similar in principle to that already suggested by Friedheim and Michaelis[6] for separating arsenic from certain other elements. Seemann[7] has made a comparative and critical study of the various methods which have been suggested for the estimation of silica and fluorine and for their separation, and recommends for the latter purpose the precipitation of the silica by mercuric ammonium carbonate. For the estimation of the fluorine, he finds that the methods of Fresenius, Brandl, Oettel, Carnot, and Offermann are all capable of giving good results. Schuch[8] has also investigated the various methods for the estimation of fluorine and favours those of Offermann and of Hempel and Schifferer. The analysis of natural silicates is frequently beset with many difficulties, and the errors inherent in the text-book methods when applied to such products are often far from inconsiderable. Jordis and Ludewig[9] deal with this subject in two papers which will be studied with interest by all chemists who have to make such analyses, and in which they discuss a number of sources of error and indicate the precautions

[1] *Analyst*, 1905, **30**, 306. [2] *Ber.*, 1905, **38**, 193. [3] *Ibid.*, 783.
[4] *J. Chem. Metall. Mining Soc. S. Africa*, 1905, **5**, 165; **6**, 36.
[5] *Arch. Sci. phys. nat.*, 1905, [iv], **19**, [4], 364.
[6] *Ber.*, 1895, **28**, 1414. [7] *Zeit. anal. Chem.*, 1905, **44**, 343.
[8] *Zeit. land. Versuch. Wes. Ost.*, 1905, **9**, 531.
[9] *Zeit. anorg. Chem.*, 1905, **45**, 362; **47**, 180.

which must be taken if accurate results are to be obtained. For the separation of silica from tungsten trioxide, as, for example, in the analysis of silicotungstates, Friedheim, Henderson, and Pinagel[1] recommend the volatilisation of the tungsten by heating to redness in a current of dry hydrogen chloride, a method which is said to give very exact results. Spielmann[2] describes the methods he has adopted for the analysis of graphitic silicon and siloxicon. The siloxicon results are interesting, as this substance, which is of some technical importance, does not appear to have been previously subjected to a detailed analysis.

Although some very useful work has been done during the year in the field of electro-chemistry as applied to chemical analysis, last year's rate of progress has scarcely been maintained. Every worker in this branch of analytical chemistry knows how greatly success depends on the nature and arrangement of the apparatus employed, and it may not be out of place therefore to call attention to a very useful paper dealing with electro-analytical methods by Puschin and Trechzinsky,[3] even although this appears to contain very little that is really new. Perkin and Prebble[4] and Root[5] deal with the electrolytic estimation of cobalt; Law and Perkin[6] with the estimation of antimony; Jene[7] with the estimation of zinc, and Spitzer[8] with the electrolytic separation of copper and zinc from cyanide solutions. Chilesotti and Rozzi[9] have studied the conditions necessary for the electrolytic estimation of molybdenum in solutions of molybdates. The employment of rotating electrodes has marked a great advance in electro-chemical procedure, and a number of estimations and separations which could not formerly be carried out electrolytically are now capable of being performed with ease, rapidity, and accuracy. By the use of a rotating anode, Davison[10] has obtained very good results in the estimation of cadmium and in its separation from magnesium and iron. The same metal has also been submitted to a detailed electrolytic study by Flora,[11] who, however, employed a rotating cathode in his experiments. R. O. Smith[12] has obtained rapid and good results in the estimation of lead by using a rotating cathode, and of mercury[13] by means of a rotating anode. Kollock and E. F. Smith[14] find that a number of metals can be very conveniently and rapidly estimated electrolytically

[1] *Zeit. anorg. Chem.*, 1905, **45**, 396. [2] *J. Soc. Chem. Ind.*, 1905, **24**, 654.
[3] *J. Russ. Phys. Chem. Soc.*, 1905, **37**, 392.
[4] *Trans. Faraday Soc.*, 1905, **1**, 103. [5] *J. Physical Chem.*, 1905, **9**, 1.
[6] *Trans. Faraday Soc.*, 1905, **1**, 262. [7] *Chem. Zeit.*, 1905, **29**, 803.
[8] *Zeit. Elektrochem.*, 1905, **11**, 345, 351.
[9] *Gazzetta*, 1905, **35**, i, 228. [10] *J. Amer. Chem. Soc.*, 1905, **27**, 1275.
[11] *Amer. J. Sci.*, 1905, [iv], **20**, 268. [12] *J. Amer. Chem. Soc.*, 1905, **27**, 1287.
[13] *Ibid.*, 1270. [14] *Ibid.*, 1255.

by using a rotating anode in combination with a mercury cathode. In this way, accurate results were obtained in a few minutes in the case of zinc, copper, nickel, cobalt, chromium, and iron.

Organic Analysis.

There is as a rule but little of importance to chronicle in the domain of qualitative organic analysis, many of the published papers dealing with the detection of special substances which are frequently of but little practical importance, and being devoted to the description of colour reactions which often depend for their success on the purity of the substance to be tested for, a condition which is not easily observed in ordinary laboratory practice. Thus, Guérin[1] describes certain colorations which are produced by the combined action of concentrated sulphuric acid and furfuraldehyde on a number of alcohols and other hydroxylic compounds, whilst Alvarez records certain colour reactions given by polyphenols and their isomerides. Aloy and Laprade[2] recommend the use of a neutral solution of a uranyl salt as a useful test for the phenolic group, a reaction being obtained in all cases except when several negative groups are also present in the compound. For the purpose of distinguishing between primary, secondary, and tertiary alcohols, Sabatier and Senderens[3] describe a simple method based on the catalytic decomposition of the alcohols by heated metallic copper and the recognition by special tests of the resulting products. Scudder[4] has usefully compared the delicacy of the various methods which have from time to time been proposed for the detection of methyl alcohol, especially in the presence of a large excess of ethyl alcohol, and appears to favour the resorcinol test. In regard to reactions of the carbohydrates, it will only be necessary to refer to two communications, one by R. and O. Adler[5] on the furfurylaniline and other tests, and the second by Sherman,[6] who has very carefully worked out the conditions under which the Barfoed test must be applied if it is to yield definite and useful indications. In connection with tests for special substances, reference may perhaps be made to a paper giving a characteristic reaction of "stovaine," by Zernik,[7] and to one by Riedel[8] dealing with the identification of lecithin, as these substances are of somewhat general interest. Green[9] has published a most useful paper dealing with the identification of colouring

[1] *J. Pharm. Chim.*, 1905, [vi], 14.
[2] *Bull. Soc. chim.*, 1905, [iii], **33**, 860.
[3] *Ibid.*, 263.
[4] *J. Amer. Chem. Soc.*, 1905, **27**, 892.
[5] *Pflüger's Archiv*, 1905, **106**, 323.
[6] *Amer. Sch. Mines Quarterly*, 1905, **26**, 159.
[7] *Apoth. Zeit.*, 1905, **20**, 174.
[8] *Ibid.*, 92.
[9] *J. Soc. Dyers Col.*, 1905, **21**, 236.

matters on animal fibres, which cannot fail to be of great assistance to chemists who are concerned with this troublesome and complicated branch of analytical chemistry. For the estimation of certain organic dyes capable of yielding colourless leuco-compounds, Knecht and Hibbert [1] recommend titration with titanous chloride, and show that in a number of cases accurate results can be obtained. Dennstedt [2] calls attention to the simplified method of elementary organic analysis which was first described by him in 1902.[3] He gives an account of a device intended to prevent the formation of explosive gaseous mixtures in the combustion tube and points out that his process not only gives good results with many organic compounds which are known to be difficult of combustion, but also that it is applicable to a number of technical products which are very troublesome to deal with by the ordinary method. It seems probable that before very long electricity will replace gas in many laboratories as a source of heat in organic combustion operations, and in the second of the papers by Dennstedt above referred to a special form of the Heraeus electric furnace is recommended. Blount [4] has also called attention to the convenience of electric furnaces in many laboratory operations. In this connection a paper by Morse and Taylor [5] may be referred to, in which an electrical method for the combustion of organic compounds is described, which is stated to possess several marked advantages over the ordinary process. A method for enabling organic combustions to be performed automatically is detailed by Pregl,[6] who states that when using it no personal attention is necessary during the actual combustion process. Pringsheim and Gibson [7] have modified the sodium peroxide process as devised by the first-mentioned author [8] for the estimation of halogens in organic compounds in such a way as to render the operation much simpler and less tedious. They find that accurate results are obtained by its employment in the case of refractory substances which are only decomposed with the greatest difficulty in the Carius method, and it seems clear that sodium peroxide is destined to be somewhat widely employed in the future in elementary organic analysis. For the estimation of sulphur, halogens, and phosphorus by the alkaline ignition method, Sadtler [9] recommends the use of a method involving the employment of two crucibles, the one within the other, which renders the method applicable to certain more or less volatile substances for which the simpler process is not available, and Garrett

[1] *J. Soc. Dyers Col.*, 1905, **21**, 3; and *Ber.*, 1905, **38**, 3318.
[2] *Chem. Zeit.*, 1905, **29**, 52; and *Zeit. angew. Chem.*, 1905, **18**, 1134.
[3] *Zeit. anal. Chem.*, 1902, **41**, 525.
[4] *Analyst*, 1905, **30**, 29.
[5] *Amer. Chem. J.*, 1905, **33**, 591.
[6] *Ber.*, 1905, **38**, 1434.
[7] *Ibid.*, 2459.
[8] *Amer. Chem. J.*, 1904, **31**, 386.
[9] *J. Amer. Chem. Soc.*, 1905, **27**, 1188.

and Lomax[1] have adopted a very similar method for the estimation of sulphur in petroleum and bituminous minerals.

It will be remembered that some difference of opinion has existed as to the applicability of the Kjeldahl method to the estimation of the nitrogen in such substances as creatine, creatinine, and lysine, both Sörensen and Pedersen[2] and Gibson[3] having maintained, contrary to the statement of Kutscher and Steudel and others, that good results could be obtained. This matter has been further investigated by Sörensen and Andersen,[4] who find that the above-mentioned and allied substances can be divided into two classes, those capable of yielding a cyclic compound containing four carbon and one nitrogen atoms, and those containing or capable of forming rings with five carbon and one nitrogen atoms, such as pyridine, piperidine, and lysuric acid. The former can be accurately analysed by the ordinary Kjeldahl method, whilst the latter give low results, but yield the whole of their nitrogen as ammonia when the process as modified by Gunning or Arnold is employed. The bearing of these observations on the analysis of substances containing or consisting of the decomposition products of proteids will be apparent. Flamand and Prager[5] describe a modification of the Kjeldahl method which renders it applicable to the analysis of azo-, azoxy-, and hydrazo-compounds. For the estimation of nitrogen in amino-acids, Staněk[6] has proposed a gasometric process based on the decomposition of nitrosyl chloride by the amino-acids and the measurement of the evolved nitrogen. In the case of glycocol, leucine, tyrosine, glutamic acid, and aspartic acid, the results are very satisfactory, but it is unfortunate that under the same conditions ammonium salts, gelatine, urea, and certain other nitrogen-containing compounds which often accompany the amino-acids in plant and animal products also yield some of their nitrogen. Betaine and some of the alkaloids do not, on the other hand, appreciably affect the accuracy of the method. For the estimation of acetyl groups, Sudborough and Thomas[7] propose a direct method which is very simple and which is stated to give good results in a number of cases. In this connection, attention may be drawn to the complete paper on the same subject by A. G. Perkin[8] to the abstract of which brief reference was made in last year's report. Lloyd[9] has studied the formation of tribromophenol bromide in Koppeschaar's bromine method for estimating phenol and shows how the errors due to this secondary reaction can be avoided. Leach and Lythgoe[10] have

[1] *J. Soc. Chem. Ind.*, 1905, **24**, 1212.
[2] *Zeit. physiol. Chem.*, 1903, **39**, 513.
[3] *J. Amer. Chem. Soc.*, 1904, **26**, 105.
[4] *Zeit. physiol. Chem.*, 1905, **44**, 429.
[5] *Ber.*, 1905, **38**, 559.
[6] *Zeit. physiol. Chem.*, 1905, **46**, 263.
[7] *Proc.*, 1905, **21**, 88.
[8] *Trans.*, 1905, **87**, 107.
[9] *J. Amer. Chem. Soc.*, 1905, **27**, 7, 16.
[10] *Ibid.*, 964.

based on the great differences in the refractive indices of ethyl and methyl alcohols a very useful refractometric method for the detection and estimation of the latter in the presence of the former. In this connection, attention may be directed to a paper by Fendler and Mannich,[1] who claim that by distillation, oxidation, and the application of the morphine test as little as 0·5 per cent. of methyl alcohol in spirit preparations can be detected. It is worthy of note that the resorcinol method of Mulliken and Scudder has, with some modification, been officially adopted for the same purpose in the new edition of the United States Pharmacopœia.

The assay of solutions of formaldehyde is a matter of some commercial importance, and both Williams [2] and Haywood and Smith [3] have devoted attention to the accurate estimation of that substance. The first-named author has investigated the best known processes and recommends those of Romijn and of Blank and Finkenbeiner according to the strength or purity of the solution under examination. Haywood and Smith have studied the latter process in detail and indicate the conditions which must be observed if uncertain results are to be avoided, whilst Fresenius and Grünhut [4] also review the various methods and arrive at substantially the same conclusions as Williams. Instead of titrating the excess of alkali in the Blank and Finkenbeiner process, Frankforter and West [5] propose a gasometric method based on the measurement of the hydrogen formed in the reaction, which appears to be capable of giving good results, although it does not possess any obvious advantages over the older titrimetric method. Messinger's iodoform method for the estimation of acetone has been criticised by Vaubel and Scheuer,[6] who recommend that the excess of iodine should be titrated with arsenious acid instead of thiosulphate, but Keppeler [7] states that the latter substance is capable of giving quite satisfactory results if steps are taken to prevent the conversion of any of the thiosulphate into sulphate. The above papers are of special interest, inasmuch as they direct attention to a matter of very considerable importance to the analyst in many connections, namely, the action of iodine on alkalis, a subject which has already been somewhat exhaustively dealt with by Foerster and Gyr.[8] Schultze [9] has made a comparative study of the best known methods which have been proposed for the estimation of glycerol in soaps, fats, distilled glycerine, and other technical pro-

[1] *Vers. Ges. deutscher. Naturforscher u. Aerzte*, 1905, Sept.
[2] *J. Amer. Chem. Soc.*, 1905, **27**, 596.
[3] *Ibid.*, 1183.
[4] *Zeit. anal. Chem.*, 1905, **44**, 13.
[5] *J. Amer. Chem. Soc.*, 1905, **27**, 714.
[6] *Zeit. angew. Chem.*, 1905, **18**, 214.
[7] *Ibid.*, 464.
[8] *Zeit. Elektrochem.*, 1903, **9**, 1.
[9] *Zeit. land. Versuch. Oest.*, 1905, **8**, 155; and *Chem. Zeit.*, 1905, **29**, 976.

ducts, and arrives at the conclusion that Zeisel and Fanto's iodine process and the modified dichromate method of Richardson and Jaffé are the most reliable. Shukoff and Schestakoff [1] have proposed an extraction method for the estimation of glycerol which has the merit of being a direct process and which is stated to give good results. Landsberger [2] has tested this and speaks well of it. A number of papers on the analytical chemistry of certain fatty oils has appeared during the year, many of which, although useful, are scarcely of sufficient importance to justify special reference to them. Fendler [3] has examined a sample of sperm oil of undoubted genuineness, which, contrary to the statements of several observers, yielded over 1 per cent. of glycerol. Should this result be confirmed, it is clear that the presence of such proportions of glycerol cannot be taken to indicate adulteration with fatty oils, as has been maintained by Benedikt and Ulzer. Rakusin [4] gives the specific gravities and optical activities of a large number of vegetable oils, and Lythgoe [5] has determined the more important optical properties of castor, cod-liver, and Neat's foot oils. Fischer and Peyau [6] have investigated the Halphen reaction for cotton-seed oil and have come to the conclusion that the phytosterol test is the only reliable one for detecting that oil in lard, inasmuch as samples of cotton-seed oil can be prepared which do not respond either to the Halphen or to the Becchi test. A paper by Suzzi [7] deals with the use of mineral oil as a diluent in examining certain drying oils by the Maumené test, and is devoted to showing that olive oil is much to be preferred for such purposes. Richardson and Hanson [8] have dealt with the valuation of lubricants in a paper which contains some new points, and which will be read with interest by chemists who are interested in the examination of those materials. For the volumetric estimation of reducing sugars by Fehling's solution, Ling and Rendle [9] recommend the use of ferrous thiocyanate as an indicator. That a solution of this substance when properly prepared does constitute a most useful indicator is the experience of many who have tried it, and its employment very considerably increases the accuracy of the volumetric method. Baker and Dick [10] have submitted the osazone method of Grimbert for the detection of small quantities of maltose in presence of dextrose to a critical examination, and find that even when improved it is not capable of detecting maltose with certainty when the proportion of that substance falls appreciably below 15 per cent.

[1] *Zeit. angew. Chem.*, 1905, **18**, 294.
[2] *Chem. Rev. Fett. Harz Ind.*, 1905, **12**, 150.
[3] *Chem. Zeit.*, 1905, **29**, 555. [4] *J. Russ. Phys. Chem. Soc.*, 1905, **37**, 442.
[5] *J. Amer. Chem. Soc.*, 1905, **27**, 887.
[6] *Zeit. Nahr. Genussm.*, 1905, **9**, 81. [7] *Boll. Chim. Farm.*, 1905, **44**, 301.
[8] *J. Soc. Chem. Ind.*, 1905, **24**, 315. [9] *Analyst*, 1905, **30**, 182. [10] *Ibid.*, 79.

of the mixed sugars. They find that the best results are obtained by taking advantage of the selective fermentation brought about by *Saccharomyces Marxianus*. This yeast has been applied to the estimation of the free sugars in starch-glucose syrups by von Raumer,[1] who calls attention to the marked effect produced on the so-called dextrins in these products by the ordinary top-fermentation yeast from German breweries, and to the consequent inaccuracy of the results obtained by fermentation methods in which such yeast has been used. A paper such as this is very useful at a time when there is a tendency to employ "biological" methods in the analysis of sugar products without any attempt to check the purity or even to ascertain the precise chemical properties of the living "reagent" employed. Ellett and Tollens[2] have endeavoured to devise a method for the estimation of methylpentosan in presence of pentosans by separating by means of alcohol the mixed phloroglucides obtained in the distillation method. Although the results are not altogether satisfactory, the process constitutes an advance and may perhaps serve as the foundation of an accurate method. Van Ekenstein and Blanksma[3] have described methods for partially separating dextrose from lævulose by converting these sugars into their respective *o*-nitrophenylhydrazones. *o*-, *m*-, and *p*-Nitrophenylhydrazines can be used for the estimation of a number of aldehydes and ketones, and it seems probable that these substances will be found to be of further service in the analysis, qualitative if not quantitative, of sugar mixtures. An ever-increasing amount of attention is being paid to the chemical examination of essential oils, and the number of papers dealing with this important branch of analytical chemistry and published during the past year is very large. As a rule, however, the authors merely record the composition and analytical "constants" of new products or describe new forms of adulteration, and whilst such communications are often of the highest importance to those analysts who are concerned with the testing and evaluation of essential oils they rarely contain matter of sufficient originality to justify special reference in a report which has necessarily to be kept within narrow limits. Much useful work of this character has been, as usual, carried out in Schimmel's laboratories and is described in their half-yearly reports. Conduché[4] finds that many aldehydes condense with *iso*hydroxycarbamide, forming well-defined crystalline compounds, which should in some cases be of service in the detection and identification of some of the aldehydic substances occurring in essential oils. Romeo[5] has described a new method for the estimation of citral in lemon oil, depending on the

[1] *Zeit. Nahr. Genussm.*, 1905, **9**, 705.
[2] *J. Landw.*, 1905, **53**, 13.
[3] *Rec. trav. chim.*, 1905, **24**, 33.
[4] *Compt. rend.*, 1905, **140**, 434.
[5] *Chem. and Druggist*, 1905, **77**, 408.

reduction of acidity which occurs when citral is absorbed by a solution of potassium sulphite or bisulphite to which an excess of the acid sulphite has been added. The test analyses are good, and it is interesting to note that the results obtained by this method, when applied to several samples of oil of lemon, support the contention of those chemists who have consistently maintained that the 7 per cent. standard so long adopted by the Messina analysts is much too high. This appears to have also been recognised by the authors of the new edition of the United States Pharmacopœia. In this connection, a paper by Sadtler [1] on the neutral sulphite method for estimating aldehydes and ketones will be read with interest. It is noteworthy that the method of Romeo and the similar one of Sadtler are criticised adversely by Schimmel [2] on the ground that it is exceedingly difficult to get an exact end-point in titration. Berté [3] has also proposed an indirect polarimetric method for the estimation of lemon oil aldehydes, which appears likely to be of use in the analysis of terpeneless lemon oils. Winton and Bailey [4] describe a further modification of Hess and Prescott's method for the analysis of vanilla extract, which appears to permit of the more accurate estimation of the coumarin. The employment of highly refined pine resin oil and other products of very similar composition to turpentine itself for the adulteration of that substance has in many cases enormously increased the difficulty of detecting sophistication, and the ordinary text-book methods which have been for so long in use are often quite inadequate. Fractional distillation under reduced pressure followed by a careful chemical and physical examination of the various fractions must frequently be resorted to if definite indications are to be obtained. Of several papers on this subject which have appeared during the year it is only necessary to mention two, both of which may be referred to with advantage. The first is by Valenta,[5] who deals chiefly with the detection of rosin spirit and pinewood oils, and the second by Utz.[6] The adulteration of shellac with rosin has now reached such serious proportions that a paper by Langmuir,[7] dealing very fully with the detection of such adulteration, will be studied with much interest by all who are called on to examine shellacs or the varnishes prepared from them. The method proposed in 1903 by Weber[8] for the analysis of india-rubber and india-rubber goods, which depended on the formation of a compound of caoutchouc with nitrogen peroxide, has been further examined by Harries [9] and by Alexander.[10] Neither of these authors has been able

[1] *J. Amer. Chem. Soc.*, 1905, **27**, 1321.
[2] *Report*, Oct./Nov., 1905.
[3] *Chem. Zeit.*, 1905, **29**, 805.
[4] *J. Amer. Chem. Soc.*, 1905, **27**, 719.
[5] *Chem. Zeit.*, 1905, **29**, 807.
[6] *Chem. Rev. Fett. Harz Ind.*, 1905, **12**, 99.
[7] *J. Soc. Chem. Ind.*, 1905, **24**, 12.
[8] *Ber.*, 1903, **36**, 3103.
[9] *Ibid.*, 1905, **38**, 87.
[10] *Ibid.*, 181.

to confirm Weber's statement as to the composition of the product, and it would seem therefore to be a somewhat risky process to employ for the estimation of caoutchouc, although it appears to be capable of giving useful results in some cases. No year passes without a number of new alkaloidal colour reactions being described. Whilst some of these are often useful, the utility of many is frequently considerably diminished by the fact that the indications are masked or rendered very uncertain by the presence of such traces of impurities as are usually present in the isolated alkaloids obtained in ordinary laboratory practice. Reichard, who has manifested great activity in this department of analytical chemistry, describes new reactions for quinine and cinchonine,[1] for sparteine, nicotine, and coniine,[2] and for aconitine,[3] whilst Alvarez[4] also records a new test for the last-mentioned alkaloid. The estimation of morphine, more especially in connection with the assay of opium, is a matter which has engaged the attention of numerous chemists, and the number of processes put forward at various times is very large. During the past year, papers on this subject have appeared by A. & A. Petit,[5] who deal with the method recommended for adoption as official in the new edition of the French Codex and who agree with Dott and Hesse as to the retention by morphine of 1 molecule of water of hydration, even after prolonged drying at 100°; by Lenton,[6] who describes a modification of the B.P. process, and by Mallinckrodt, jun., and Dunlap.[7] The last-named authors, in a paper which deals at some length with the chemistry of meconic acid and the meconates, describe a calcium ammonium meconate which appears to be formed during the assay of opium by the U.S. Pharmacopœia (1890) method. The chief importance of this observation to the analyst lies in the fact that this salt neutralises one-fourth as much acid as morphine itself, and that its presence consequently vitiates the titration results for that alkaloid. Several papers on the estimation of quinine have appeared, but these do not contain much that is new or of importance. Reference may perhaps be made in passing to the suggestion of Duncan,[8] that calcium hydroxide should be used in place of ammonia as a precipitant for the alkaloid and for titration of quinine sulphate solutions, as more accurate results are obtained. Keller's method for separating strychnine and brucine, and depending on the destruction of the latter alkaloid by sulphuric acid, has been studied by Howard,[9]

[1] *Pharm. Zeit.*, 1905, **50**, 314, 430.
[2] *Pharm. Centr.-H.*, 1905, **46**, 309; **48**, 385.
[3] *Ibid.*, **46**, 479.
[4] *Compt. rend.*, 1905, **140**, 1540.
[5] *J. Pharm. Chim.*, 1905, **21**, 107.
[6] *Pharm. J.*, 1905, **74**, 652.
[7] *J. Amer. Chem. Soc.*, 1905, **27**, 946.
[8] *Pharm. J.*, 1905, **74**, 438.
[9] *Analyst*, 1905, **30**, 261.

who finds that if care be taken to keep the temperature sufficiently low, good results are obtained and that any such modification of the process as that recently proposed by Gordin is not necessary. Thomas [1] describes a method for estimating alkaloids which involves their separation by the ordinary potassium bismuth iodide reagent, and states that when applied to the estimation of belladonna alkaloids good results were obtained. For the estimation of the active principles of alder bark and cascara sagrada, Warin [2] describes a colorimetric method which appears to be useful.

Staněk [3] has continued his study of the potassium tri-iodide method for the estimation of betaine, and finds that under proper conditions it may be usefully applied to the examination of industrial sugar products. The procedure to be adopted for the separation of betaine from other co-precipitated nitrogenous substances is described, and the work appears appreciably to advance our knowledge of the impurities present in certain products of the sugar factory. H. Wislicenus [4] has further investigated the applicability of his highly porous ("spongy") alumina to the analysis of tanning materials, and claims that more concordant results are obtained than by the hide-powder process. This claim appears, however, to Paessler [5] to need further confirmation, and he suggests that the method should be submitted to a more thorough and searching investigation. In this connection, it is of interest to note [6] that the Commission appointed by the International Association of Leather Trades Chemists to investigate the candle-filter method of Parker and Payne [7] has reported in favour of substituting such a filter for paper in the analysis of tannin solutions. Both the above matters are dealt with by Weiss,[8] who criticises Wislicenus' method adversely, and does not altogether approve the use of a candle-filter. This paper also contains a criticism of Parker and Payne's titration method and a description of the author's chromed hide-powder process as practised at the Vienna Research Institute. Trotman and Hackford [9] recommend the use of strychnine as a precipitant of tannic acid. This suggestion marks a distinct advance in the analysis of tannin-containing materials, inasmuch as it involves the substitution of a definite chemical reagent for the indefinite materials at present employed. The further development of this work will be watched by all leather chemists with very considerable interest.

[1] *Ber. Deut. pharm. Ges.*, 1905, **15**, 85.
[2] *J. Pharm. Chim.*, 1905, **21**, 253; **22**, 12.
[3] *Zeit. Zuckerind. Böhm.*, 1905, **29**, 410.
[4] *Zeit. anal. Chem.*, 1905, **44**, 96.
[5] *Ibid.*, 301.
[6] *Collegium*, 1905, 46.
[7] *Ibid.*, 1904, 249.
[8] *Der Gerber*, 1905, **31**, 260, 275.
[9] *J. Soc. Chem. Ind.*, 1905, **21**, 1096.

Analysis of Food and Drugs.

Of all the articles which are, or may be, submitted to public analysts under the provisions of the Sale of Food and Drugs Acts, milk is unquestionably the most important from the point of view of the well-being of the community, and a very special interest attaches therefore to any investigation bearing either on its composition or on its analytical examination. In reviewing the work of the past year in connection with this food product, a foremost position must be assigned to a paper by T. E. Thorpe[1] on the analysis of samples of milk referred to the Government Laboratory in connection with the Sale of Food and Drugs Acts. Such samples have, of course, invariably undergone more or less decomposition when received, and it has naturally been of importance to determine whether that fact prevents a correct inference as to the character of the milk or interferes with a determination of the degree of sophistication to which it may have been subjected. The communication in question deals very fully with the nature of the more important chemical changes occurring during the souring of milk, and contains an account of numerous experiments made for the purpose of ascertaining the relation existing between the decomposition products present in any sample and the original milk constituents from which they had been formed. As a result of this important work, it has been found possible to "reconstitute" the original sample with a remarkable degree of accuracy, and to obtain results in the analysis of sour milks which agree very closely indeed with those given by the same samples when in a fresh condition. In connection with the decomposition of milk and the estimation of ammonia formed by the decomposition of the proteids, reference may be made to a paper by Berg and Sherman.[2] Another paper of importance to food analysts is Richmond's annual communication on the composition and analysis of milk.[3] In this he states that the average percentage of fat in more than 33,000 samples analysed during 1904 was found to be 3·74 per cent., and of non-fatty solids 8·94 per cent. It is interesting to note in this connection that Billitz[4] finds almost exactly the same average proportion of non-fatty solids (8·81 per cent.) in 187,610 samples of Lombardy milk analysed during the years 1892—1902 inclusive, but gives as the average fat percentage 3·55 per cent., which is a little lower. Richmond's paper above referred to contains some useful information in reference to the estimation of milk fat by the Gerber process, and the attention of analysts may be directed to another com-

[1] *Trans.*, 1905, **87**, 206.
[2] *J. Amer. Chem. Soc.*, 1905, **27**, 124.
[3] *Analyst*, 1905, **30**, 325.
[4] *Milchw. Zentr.*, 1905, **1**, 113.

munication by the same author and Goodson,[1] which indicates the importance of submitting the amyl alcohol used in centrifugal methods of fat estimation to a more searching examination than has hitherto been considered necessary. Watts and Tempany[2] find that certain constituents of milk exert a retarding influence on the inversion of cane sugar by means of citric acid, and that for the estimation of that sugar in condensed milks and similar products it is necessary to prolong the inversion period considerably beyond that originally recommended by Stokes and Bodmer. Owing to the comparatively large proportion of the glycerides of volatile fatty acids in cocoa-nut oil, the employment of that fat for the manufacture of margarine and for the direct or indirect falsification of butter has very considerably increased the difficulties of the analyst. In my previous report I called attention to the methods of Muntz and Coudon and of Polenske for its detection and estimation, methods based upon a differentiation of the volatile insoluble from the volatile soluble fatty acids obtained in the Reichert-Meissl process. Experience of these methods has shown that they are capable of yielding exceedingly useful indications in many cases of adulteration in which the ordinary methods of butter analysis would have been of little use, but a good deal of work still remains to be done before the problem can be considered to have been satisfactorily solved. The method of Polenske has been subjected to examination by Hesse,[3] who calls attention to several details of procedure which must be observed if uniform results are to be obtained. It is also pointed out that the "new butter value" is somewhat considerably affected by changes in the feeding of the cows which scarcely affect the Reichert-Meissl value at all. A very useful contribution to this subject comes from Kirschner,[4] who has described for the estimation of butter-fat and cocoa-nut oil in margarine a modification of the process first published by K. Jensen.[5] This is based on the different proportions in which octoic and butyric acids occur in the Reichert-Meissl distillates from the above fats, and on the comparative insolubility of silver octoate in water. It appears that this process has been for some time in regular use in at least one well-known continental laboratory, and it has been favourably reported on and more fully worked out by O. Jensen.[6] It seems not improbable that an extended investigation of the solubilities in water of the silver salts of certain of the volatile fatty acids, separately and mixed, on the lines already followed by O. Jensen[7] would be of considerable value in connection with the analysis of adulterated butters. The method of Jensen and Kirschner is, however, based on

[1] *Analyst*, 1905, **30**, 77.
[2] *Ibid.*, 119.
[3] *Milchw. Centr.*, 1905, **1**, 13.
[4] *Zeit. Nahr. Genussm.*, 1905, **9**, 65.
[5] *Farm. Tid.*, 1903, 385.
[6] *Zeit. Nahr. Genussm.*, 1905, **10**, 265.
[7] *Loc. cit.*

certain well-defined differences in the chemical composition of the above-mentioned fats, and further investigations on these lines are sure to be forthcoming, and will be studied with considerable interest when they appear. As a further contribution to the subject, Wauters [1] has recorded the different appearances of the crystals of cocoa-nut oil and butter-fat as observed by means of the microscope with and without polarised light. Hoton [2] has published a further paper dealing with the application of the different solubilities of various glycerides in acetic acid to the analysis of butter, and shows that useful indications can be obtained. It does not, however, appear to be susceptible of application to the detection of cocoa-nut oil. For the recognition of small quantities of sesamé oil in butter, Sprinkmeyer and Wagner [3] recommend an apparently useful procedure in which the substances giving the Baudouin colour reaction are concentrated, and which is said to be capable of detecting as little as 0·1 per cent. of sesamé oil with certainty. The attention of food analysts may be directed to a paper by Wesson and Lane [4] on the analysis of lard. It is true that this contains little that is novel, but it summarises very usefully the methods which are capable of giving the most reliable results, and contains an account of one or two which are better known in America than elsewhere. Emmett and Grindley [5] have shown that the lard obtained from pigs fed on cotton-seed meal responds to a number of the general tests for vegetable oils, and gives the more important special reactions of cotton-seed oil. They also isolated from such lards crystals resembling those of phytosterol, but Tolman, who has been working on the same subject,[6] has been unable to confirm this. The nature of the substance giving the red coloration in the very useful test bearing his name has been investigated by Halphen,[7] who arrives at the conclusion that it is an unsaturated acid, and that the colour is not due, as has been asserted by Raikow, to the formation of a thio-derivative. Proctor [8] has described a new and apparently exact method for the estimation of saccharin based on the fact that both the ortho- and para-benzoylsulphonimides liberate iodine quantitatively from a solution containing iodide and iodate of potassium. The increasing use of chemical substances for the preservation of articles of food, and the necessity of keeping a rigid control over this practice in the interest of public health, has rendered the detection and estimation of such substances an important part of the daily work of the food analyst.

For the detection of formaldehyde in milk, new reactions have been

[1] *Bull. Soc. chim. Belg.*, 1905, **19**, 6.
[2] *Rev. intern. Falsif.*, 1905, **18**, 20.
[3] *Zeit. Nahr. Genussm.*, 1905, **10**, 347.
[4] *J. Soc. Chem. Ind.*, 1905, **24**, 714.
[5] *J. Amer. Chem. Soc.*, 1905, **27**, 263.
[6] *Ibid.*, 589.
[7] *Bull. Soc. chim.*, 1905, [iii], **33**, 108.
[8] *Trans.*, 1905, **87**, 242.

described by Utz,[1] Bonnet, jun.,[2] Nicolas,[3] and others; but whilst as a rule great sensitiveness is claimed for these, it seems doubtful whether they possess any clear advantage over the well-tried method of Hehner, or the similar one in which the sulphuric acid is replaced by hydrochloric acid. They may, however, be useful in certain cases as confirmatory tests. It may be noted that Lyons[4] has modified Hehner's formaldehyde test in order to make it applicable to other substances than milk, and claims that by using beef peptone as the proteid material one part of formaldehyde in 4,000,000 can be detected. In a paper on the colorimetric estimation of salicylic acid in food-stuffs, Harry and Mummery[5] describe a process which avoids the difficulty often experienced in obtaining a good colour with ferric chloride, and which is particularly applicable to certain fruit pulps and other products which contain appreciable quantities of tannin and similar substances capable of giving colour reactions with the iron solution. For many purposes, this method appears to mark a great advance on the ordinary direct extraction with ether and light petroleum. Archil and cudbear are not infrequently used for the purpose of colouring articles of food in cases where the use of coal-tar dyes is prohibited. Tolman[6] points out that these and other lichen colours may easily be mistaken for the coal-tar dyes, and describes a method for distinguishing between them. Several papers have appeared during the year dealing with the analytical examination of vinegar, and of these reference may be made to those of Froehner,[7] Pastureau,[8] and Rossi.[9] The first-mentioned author records some analyses of wine vinegar, and points out that the presence of lactic acid in such vinegar affords a useful indication of its origin and serves to differentiate it from vinegars derived from other sources. The detection by Pastureau of appreciable quantities of acetylmethylcarbinol in several samples o grain vinegar is interesting, but it may be doubted whether his suggestion of its bacterial origin is the correct one. Rossi calls attention to the fact already pointed out by Schidrowitz,[10] that free sulphuric acid can be directly titrated in vinegar, using methyl-orange as indicator, if alcohol or acetone are first added. In a paper by Windisch and Roettgen,[11] attention is called to the appreciable volatility of lactic acid with steam and to the error thus introduced into the estimation of the volatile acids in wine by distillation. This property of lactic acid is also dealt with by Utz,[12] and is clearly of considerable import-

[1] *Chem. Zeit.*, 1905, **29**, 669.
[2] *J. Amer. Chem. Soc.*, 1905, **27**, 601.
[3] *Compt. rend.*, 1905, **140**, 1123.
[4] *Pharm. J.*, 1905, **75**, 443.
[5] *Analyst*, 1905, **30**, 124.
[6] *J. Amer. Chem. Soc.*, 1905, **27**, 25.
[7] *Zeit. Nahr. Genussm.*, 1905, **9**, 361.
[8] *J. Pharm. Chim.*, 1905, [vi], **21**, 593.
[9] *Zeit. Nahr. Genussm.*, 1905, **9**, 698.
[10] *Analyst*, 1903, **28**, 233.
[11] *Zeit. Nahr. Genussm.*, 1905, **9**, 70.
[12] *Chem. Zeit.*, 1905, **29**, 363.

ance in view of the fact that, as a general rule, the non-volatility of lactic acid is assumed in analytical procedure. In the estimation of glycerol in wines, Rocques [1] recommends the use of a mixture of alcohol and ethyl acetate for extraction, a mixture which, while dissolving glycerol readily, is said to exert very little solvent action on the other wine constituents. A modification of the alcohol-ether method has also been proposed by Laborde.[2] The estimation of the so-called higher alcohols in potable spirits is an analytical problem beset with many difficulties, and one which has certainly not been as yet satisfactorily solved. Schidrowitz and Kaye [3] have very usefully undertaken a critical examination of several of the better known methods, and give the preference to the Allen-Marquardt process as being the most reliable. Beckmann's nitrite process is adversely criticised, but it is to be noted that Beckmann [4] has now modified his original method, which may consequently be capable of yielding more accurate results. A great advantage of the Allen-Marquardt process, however, consists in the fact that the actual oxidation products of the higher alcohols are obtained and can be used for purposes of examination or identification. Numerous papers dealing with the analysis of drugs have been published during the year, but these, whilst often very useful, are scarcely of sufficient general interest or importance to justify special reference in this Report. In view of the increasing importance of adrenaline as a therapeutic agent, attention may be called to a paper by Abelous, Soulié, and Toujan [5] on the colorimetric determination of that substance and its estimation in suprarenal glands. Bourcet [6] describes a test which is capable of detecting as little as 2 per cent. of antipyrin in pyramidone (dimethylamino-antipyrin), which appears useful in view of the somewhat frequent adulteration of the latter drug with the much cheaper antipyrin.

A new gravimetric method for the estimation of pyramidone is also given by Astruc and Pégurier,[7] depending on its precipitation with picric acid, and one for the approximate estimation of both drugs when present together by Patein.[8] In my previous report I had occasion to refer to the question of the detection of adulterants in cod-liver oil, a subject which, during the present year, has received some attention. Parry [9] has published the tabulated results of the analysis of forty samples of known genuineness, and his numbers should be of value to analysts who are called on to examine this oil. The methods for estimating the metallic iron in ferrum redactum, including that of

[1] *Ann. Chim. anal.*, 1905, **10**, 306.
[2] *Ann. Chim. anal.*, 1905, **10**, 340.
[3] *Analyst*, 1905, **30**, 190.
[4] *Zeit. Nahr. Genussm.*, 1905, **10**, 143.
[5] *Compt. rend. Soc. Biol.*, 1905, 301.
[6] *Bull. Soc. chim.*, 1905, [iii], **33**, 572.
[7] *Ann. Chim. anal.*, 1905, **10**, 302, 392.
[8] *J. Pharm. Chim.*, 1905, [vi], **22**, 5.
[9] *Chem. and Druggist*, 1905, **66**, 491.

the German Pharmacopœia, are criticised in a paper by Christensen,[1] who recommends a process based on the reduction of ferric to ferrous salt, whilst Barmwater[2] advocates the employment of a gasometric method.

Toxicological Analysis.

In this branch of chemical analysis there are only a few communications to which special attention need be directed. The important question of the destruction of organic matter as a preliminary to the detection and estimation of inorganic poisons has received attention at the hands of several investigators. It is clear that in some cases, more especially when arsenic and antimony have to be estimated, the employment of boiling concentrated sulphuric acid, as in Kjeldahl's nitrogen process, presents marked advantages over the methods in general use, and both Norton and Koch[3] and Grigoréeff[4] recommend this procedure, either with or without the addition of nitric acid.

For the estimation of arsenic in toxicological work, Mai[5] recommends the adoption of an electrolytic method, the organic matter being carbonised and partly oxidised by treatment with mixed nitric and sulphuric acids, and the arsenic separated from the dry carbonaceous mass by distillation with hydrochloric acid in the usual way. The arsenical distillate is then transferred to an electrolytic apparatus of special construction[6] and the evolved gas passed through a known volume of standard silver nitrate solution. From the amount of unreduced silver, the arsenic can be calculated. In the case of minute traces, the mirror method must, of course, be employed. Frerichs and Rodenberg,[7] who have worked on the same subject, describe a modified electrolytic cell which is said to enable the complete reduction of the arsenic to be effected in much less time than in the apparatus of the above-mentioned authors. It is worthy of note that in nearly all recent work on the electrolytic estimation of arsenic the use of platinum cathodes has been abandoned, owing to the far greater sensitiveness and efficiency of cathodes constructed of zinc or lead. In this connection, mention may be made of a paper by Virgili[8] containing an account of a critical examination of the magnesium pyroarsenate method for estimating arsenic. Among much which is perfectly well known to every properly trained analyst, there are some observations which

[1] *Zeit. anal. Chem.*, 1905, **44**, 535. [2] *Ibid.*, 541.
[3] *J. Amer. Chem. Soc.*, 1905, **27**, 1247.
[4] *Viertelschr. ger. Med. öffentl. Sanitätswesen.*, **29**, 74.
[5] *Zeit. Nahr. Genussm.*, 1905, **10**, 290.
[6] Mai and Hurt, *Zeit. Nahr. Genussm.*, 1905, **9**, 193.
[7] *Arch. Pharm.*, 1905, **243**, 348. [8] *Zeit. anal. Chem.*, 1905, **44**, 492.

merit the attention of chemists who have occasion to employ this process. Since hydrogen peroxide is not infrequently made use of as an oxidising agent in analytical procedure, the observation of Grimbert [1] that commercial solutions of this substance often contain appreciable quantities of arsenic is deserving of note. W. Thomson [2] has investigated the occurrence of arsenic in the human body and its secretion by the kidneys and finds that the urine of people living in districts where, owing to industrial operations, the atmosphere is contaminated with arsenic, contains appreciable traces of that substance. The presence of traces of arsenic in the urine, lungs, and hair is therefore, in such circumstances, devoid of much significance. Schumm [3] describes an electrolytic method for the estimation of small quantities of mercury in animal organs, which appears to be susceptible of useful application. A gold foil cathode is used and the mercury is easily obtained in the metallic condition for weighing and identification.

Apparatus.

In the foregoing pages of this report, reference has incidentally been made in several cases to certain improved analytical appliances, and it has not been thought necessary to draw attention to these again. The following list contains references only to those new pieces of apparatus which have been described in recognised journals, and which appear to meet a real want and to be of general utility. It may not be out of place to refer here to two papers on quartz glass apparatus by Berthelot,[4] and to one by Mylius [5] on the same subject, since there can be no doubt that this material will in the future find useful application in analytical procedure. A paper by Brill [6] on some experiences in the use of the micro-balance is also of interest.

"A compact apparatus for testing gases." R. Fieber (*Chem. Zeit.*, 1905, **29**, 80).

"A modified Orsat gas analysis apparatus." J. E. Babb (*J. Amer. Chem. Soc.*, 1905, **27**, 156). Also A. Bement (*J. Amer. Chem. Soc.*, 1905, **27**, 1252).

"Tube apparatus for drying in a current of carbon dioxide." K. Voigt (*Chem. Zeit.*, 1905, **29**, 691).

[1] *J. Pharm. Chim.*, 1905, **21**, 385.
[2] *Mem. Proc. Manchester Phil. Soc.*, **49**, 1.
[3] *Zeit. anal. Chem.*, 1905, **44**, 73.
[4] *Compt. rend.*, 1905, **140**, 817, 821.
[5] *Zeit. anorg. Chem.*, 1905, **44**, 221.
[6] *Ber.*, 1905, **38**, 140.

"An improved Hempel gas analysis apparatus." A. H. White and E. D. Campbell (*J. Amer. Chem. Soc.*, 1905, **27**, 732).

"Use of nickel vessels in analytical practice." L. L'Hôte (*Ann. Chim. anal.*, 1905, **10**, 253).

"An improved colorimeter for general use." O. Schreiner (*J. Amer. Chem. Soc.*, 1905, **27**, 1192).

"A portable gas analysis apparatus." B. Neumann (*Chem. Zeit.*, 1905, **29**, 1128).

"Gas regulators for thermostats." T. M. Lowry (*Trans.*, 1905, **87**, 1030).

"A burette for delivering the amyl alcohol in Gerber's method of fat estimation." C. Kippenberger (*Zeit. angew. Chem.*, 1905, **18**, 1025).

"An apparatus for heating substances in a vacuum at a constant temperature." W. R. Hodgkinson and A. H. Coote (*Chem. News*, 1905, **91**, 194).

"Two modifications of the Topler pump." A. Stock (*Ber.*, 1905, **38**, 2182).

"An automatic mercury pump with shortened column of mercury." L. Ubbelohde (*Ber.*, 1905, **38**, 2657).

"A simple Bunsen burner." F. Allihn (*Chem. Zeit.*, 1905, **29**, 34).

"A new form of Eggertz tube for the determination of carbon in steel and iron." H. Schumacher (*Chem. Zeit.*, 1905, **29**, 35).

"A practical mechanical mortar" (*Chem. Zeit.*, 1905, **29**, 56).

"Gas-holder with constant flow." Mario Betti (*Chem. Zeit.*, 1905, **29**, 219).

"Potash apparatus for the rapid absorption of carbon dioxide." G. Schöler (*Chem. Zeit.*, 1905, **29**, 569).

"New automatic pipette." Greiner and Friedrichs (*Zeit. angew. Chem.*, 1905, **18**, 465).

"Improved suction filter." J. Katz (*Chem. Zeit.*, 1905, **29**, 489).

"Electrically heated carbon tube furnaces." R. S. Hutton and W. H. Patterson (*Chem. News*, 1905, **91**, 272, 285).

"A new apparatus for the continuous supply of gases." Emil Geisel (*Chem. Zeit.*, 1905, **29**, 726).

"An apparatus for heating crucibles by means of electricity (electric oven) under reduced pressure." E. Haagn (*Chem. Zeit.*, 1905, **29**, 1209).

"A new apparatus for supporting crucibles during ignition intended to secure greater heating efficiency." A. Kette (*Chem. Zeit.*, 1905, **29**, 1208).

The above are not always the exact titles given by the authors, but have been in some cases slightly altered so as to indicate more clearly the nature of the apparatus in question.

In concluding this report, the author would once again remind his readers that exigencies of space have compelled him to refer only to those communications which appeared to him to be of the greatest value, either from the point of view of their practical importance or of their general scientific interest. The difficulty of making such a selection from the vast and ever-increasing amount of published matter has been very great, and the limits assigned to this review have naturally precluded reference to a considerable number of papers, many of which unquestionably embody useful observations.

ALFRED C. CHAPMAN.

PHYSIOLOGICAL CHEMISTRY.

As the report which I prepared last year on Physiological Chemistry was the first of the series, I seized the occasion to preface my summary of the year's work by some general remarks, comparing, for instance, the condition of this branch of knowledge at the present time with what it was twenty years ago, and noting the general lines on which it has progressed. In this year's report it is of course unnecessary to go over that ground again, but a study merely of the number of the abstracts appearing month by month in the Society's Journal and of their titles will indicate that there is no halt in the increasing attention which physiologists are bestowing on the chemical side of their science, and will show that many of the papers are concerned with working out and elaborating the details of most of the subjects alluded to in my report of last year.

I have next to chronicle the appearance of two new journals devoted to biochemistry. One of these has been issued in America, and is under the editorship of Dr. C. A. Herter and Prof. J. J. Abel. The early numbers of volume I of this journal have already been published. The other, edited by Prof. B. Moore and Dr. Whitley in this country, emanates from the University of Liverpool, and its first number is promised at an early date. One regrets from some points of view the ever-growing number of scientific journals, but it appears to be inevitable that with the increase of specialisation in science it should occur, and one cannot but rejoice that biochemistry is at last to be represented in scientific literature by special journals written in the English language.

In dealing with the large mass of material at my disposal, it is again necessary that I should make a selection, and I shall endeavour to choose those researches for comment which deal with broad questions, rather than those concerned with mere detail.

Proteid Chemistry and Proteid Metabolism.

Emil Fischer and his colleagues are continuing their important work on the polypeptides, but it is evident that much remains to be done before it is possible to apply the mass of knowledge thus accumulating

to the elucidation of the structure of the proteid molecule and to an attempt to synthesise albumin. As an instance of the kind of laborious work this involves, one may allude to the papers issuing from the pen of Abderhalden,[1] who, in the examination of numerous proteids, has prepared the various cleavage products and shown how different such are both in kind and in amount in the different members of the proteid family.

The physiological action of the cleavage products and the exact manner in which they are utilised in the body form a wide field for future investigation. One small gap in our knowledge in this direction I was enabled to fill through the kindness of Prof. Emil Fischer himself. It is well known that the effect "peptone" has in lessening the coagulability of the blood is mainly due to the primary proteoses it contains. W. H. Thompson some years ago pointed out that the same admixture is responsible for another physiological effect, which generally runs parallel with this, namely, the lowering of arterial blood pressure on intra-vascular injection; the further proteolysis is continued, the less do these effects manifest themselves. The crystalline cleavage products of proteolysis do not have any such physiological effect (C. G. L. Wolf),[2] and negative results were also obtained with the samples of polypeptides sent to me by Prof. Fischer.[3] The combinations of molecular groups necessary to produce such effects must therefore be more complex than the polypeptides.

This, however, is only a small point; a much more important and general question is the utilisation of the cleavage products when they are administered by the alimentary canal.

Evidence is steadily accumulating which confirms Loewi's statement that, in animals, weight, health, and nitrogenous equilibrium can be maintained for a considerable time by feeding them on the crystalline cleavage products of proteolysis. This is what one would expect if the action of the digestive ferments on the proteid constituents of food is normally carried beyond the peptone stage. The major part of the proteid ingested is now believed to undergo this extreme cleavage, and, that being so, the various proteids of the body must be formed synthetically from comparatively simple materials.

It has not been possible as yet to discover these cleavage products in the blood-stream when they are administered by the alimentary canal; the synthesis is therefore provisionally considered to occur in the absorptive epithelium of the alimentary tract. This localisation of

[1] *Zeit. physiol. Chem.*, 1905, **45**, 473, 479; *Abstr.*, 1905, i, 846; and numerous papers appearing in the current volume (vol. **46**) of *Zeit. physiol. Chem.*, some of which have been abstracted. *Abstr.*, 1905, i, 954; ii, 838, 839, 840, 843.

[2] *J. Physiol.*, 1905, **32**, 171; *Abstr.*, 1905, ii, 264.

[3] Halliburton, *J. Physiol.*, 1905, **32**, 174; *Abstr.*, 1905, ii, 265.

the place of proteid synthesis cannot, however, be taken as fully proved yet, for some experiments by Schryver[1] have not confirmed the hypothesis. Leathes[1] also attempted to discover if it is really the case by examining the blood leaving isolated loops of intestine, in the interior of which the cleavage products had been placed. These loops were perfused with defibrinated blood, but under these experimental conditions no absorption whatever occurred; one hopes that the experimental difficulties will in time be overcome.

There is something very attractive in a theory which assumes a complete breakdown of the food-stuffs previous to their being built into living tissue. It is less difficult to understand how the living organism can construct from the fragments the tissues peculiar to itself and maintain its chemical individuality, although the food taken may vary widely in composition.

Abderhalden[2] has published a very striking experiment in confirmation of this view. He collected the blood of a horse, separated out the various proteids of the plasma, and estimated in each the yield of certain cleavage products (glutamic acid and tyrosine) which resulted from hydrolysis. He then fed the horse so that it formed new blood, but the only proteid given was gliadin, a vegetable product, which is remarkable for its high percentage yield (36·5) of glutamic acid. But in the regenerated blood proteids the percentage yield of glutamic acid was not increased at all; they exactly resembled the proteids previously present.

It is a far cry from the highly specialised organism of the horse to the protoplasm of the simple mould known as *Aspergillus niger*; nevertheless, the same general rule holds; the proteid matter present yields, on hydrolysis, glycine, alanine, leucine, glutamic and aspartic acids, but aromatic products, such as tyrosine and phenylalanine, were not discovered. The mould was then cultivated on media of widely varying composition, but the proteid formed in the living protoplasm remained constant in composition, and is independent of the composition of the nutritive medium.[3]

What then, if this is the case, would be the fate of food proteids introduced directly into the blood stream without the intervention of the alimentary digestive processes? This is a question to which Mendel and Rockwood[4] have been attempting to find an answer. If the preliminary cleavage in the gastro-intestinal tract is absolutely necessary, one would anticipate that a foreign food proteid (such as edestin

[1] Verbal communications to the Physiological Society.

[2] *Zeit. physiol. Chem.*, 1905, **46**, 193; *Abstr.*, 1905, ii, 840.

[3] Abderhalden and Rona, *Zeit. physiol. Chem.*, 1905, **46**, 179—186; *Abstr.*, 1905, i, 954.

[4] *Amer. J. Physiol.*, 1904, **12**, 336; *Abstr.*, 1905, ii, 45.

from hemp seed, or excelsin from Brazil nuts) administered by intravenous or intraperitoneal injection would not be assimilated, but would be cast out of the body in one or more of the excretions. But Mendel and Rockwood found that they were not eliminated in either urine or bile. In some cases, a proteose was found in small quantities in the urine, but the greater part of the proteid administered was retained in the body, especially if the injection was slowly performed. Rapid injection causes toxic symptoms, as one would anticipate. No doubt future attempts will be made to ascertain more exactly what happens to the retained proteid and the exact mode of utilisation which it undergoes.

The fact that proteids are retained after this method of administration and apparently used in the body does not really militate against the theory that proteids under normal conditions are more or less completely broken down in the alimentary tract. Clinical experience with feeding *per rectum* indicates the possibility of a direct absorption of proteid without previous digestive changes. We have here one of many instances of the adaptability of the body to altered circumstances ; at a critical moment, various portions of the body are capable of rising to the occasion and performing unusual feats, or of taking on the action normally performed elsewhere. The usual form in which the body gets its proteid is by building it up from simple crystalline materials, but if these are not available, it can still get proteid by absorbing the large molecules of the albumin presented to it. It is more than probable, however, that cleavage is absolutely necessary for assimilation, and here the enzymes present in the tissue cells step in ; they are capable of occasionally taking the place of the pancreatic trypsin and intestinal erepsin and doing their work. The presence of a proteose in urine in some of Mendel and Rockwood's experiments points in this direction, and this view is supported also by Vernon's[1] recent discovery that every tissue of the body has an ereptic action, and that in some tissues this power is even greater than in the intestinal cavity and mucous membrane.

In last year's Report I mentioned the appearance of Professor Chittenden's book, entitled *Physiological Economy in Nutrition*. In view of work published more recently, which forms a corollary to his conclusions, it is necessary to enter more fully into the contentions of this really important book.

The long established idea that a man requires a minimum of 15 to 18 grams of nitrogen (that is, about 100 grams of proteid) in his daily food has been questioned by a number of observers, but the conclusion that a man can do with less has not been advanced con-

[1] *J. Physiol.*, 1904, **32**, 33 ; *Abstr.*, 1905, ii, 100 ; also *J. Physiol.*, 1905, **33**, 81 ; *Abstr.*, 1905, ii, 841. See also Cathcart on the splenic enzyme (*J. Physiol.*, 1905, **32**, 299 ; *Abstr.*, 1905, ii, 404).

vincingly, because the experiments have been made either over too short a period or on too few individuals. The figure quoted is based roughly on the usual diet of the meat-eating nations, and it is argued that habit and instinct alike are safe guides in determining this number, and that the effect of such a diet in the maintenance of health and equilibrium has been abundantly proved through centuries of experience. It is the number which forms the basis of the usually accepted dietaries of Voit and Ranke.

In other nationalities, it is true, a different figure has been arrived at as the result of experience and instinct; the prevalence of dyspeptic troubles and uric acid disorders in our midst also should make us hesitate before we conclude that our own diet has reached the stage of perfection. It is alleged that in such nations as the Japanese, or in groups of persons like vegetarians, and in many rural populations where low wages render meat a rarely obtained luxury, health and equilibrium are equally well maintained as in the ordinary flesh-eating inhabitants of our large cities. Those who hold that the number 15 to 18 is the correct one have explained the different number arrived at by the nations of the Far East as a racial difference propagated by long centuries of inheritance, or have tried more or less successfully to show that the diet of such people comes nearer to Voit's standard than had been supposed, or that they are not properly nourished.

Such explanations will not bear scrutiny when applied to the carefully conducted and rigorous experiments carried out by Professor Chittenden on himself, his colleagues, his students, and on athletes and soldiers. These experiments lasted in all cases for months, and in some for more than a year. The proteid intake was reduced to half, and sometimes to less than half, the number regarded as normal. After a variable initial drop in body weight, the deprivation was apparently followed by no untoward results. Bodily equilibrium was maintained; the health remained perfect or improved; the muscular force in athletes was usually increased; mental acuity was undiminished, and desire for richer food soon disappeared.

Chittenden argues from such results that his scanty proteid diet is the normal one, and that the average meat eater is the man who is abnormal. He says: "When we recollect that these 18 grams or more of nitrogen in the urine reach the final stage of urea, &c., only by passing through a series of stages each one of which means the using up of a certain amount of energy, to say nothing of the energy made use of in digestion, absorption, &c., we can easily picture to ourselves the amount of physiological labour which the daily handling by the body of such amounts of proteid entails. It needs very little imagination to see that a large amount of energy is used up in passing on

these nitrogenous waste products from organ to organ, or from tissue to tissue, on the way to elimination, and we can fancy that liver and kidneys must at times rebel at the excessive labour they are called upon to perform." He then goes on to point out how many of the nitrogenous katabolites (especially of the uric acid group) are toxic, and the evil results due to their accumulation. He therefore advocates a revolution in our ordinary dietary, and his arguments for temperance in proteid intake are advanced in a temperate and scientific manner.

Liebig was the first to divide foods into flesh forming and heat forming, that is, into those which repair the tissue waste and those which are not so intimately assimilated into the protoplasm, but are utilised as sources of energy. The latter function is the one performed by the fats and carbohydrates, and the former is more particularly the duty of the proteids. This idea is reflected in the popular use of the term nutritious; it is used almost synonymously with nitrogenous, and the notion that non-nitrogenous foods, although they form the greater part of our daily diet, are not nutritious and are next door to useless is carefully fostered by the advertisers of patent foods. It is now known that the proteids are not only flesh formers, but also that they play the other *rôle* in nutrition, and act as a source of energy. The complete breakdown of proteid matter which occurs in the gastro-intestinal tract has in fact a double signification. It enables the body to construct from the cleavage products the proteids peculiar to itself, and it further enables the body to get rid easily of the nitrogenous moiety of the proteid which is not wanted for tissue formation. It in fact protects us from the evils of the too great amount of proteid most of us eat. This portion is never really assimilated, but is rapidly converted into urea and so rendered harmless, and is quickly cast out by the kidneys. The non-nitrogenous moiety which remains is then utilised for energy and heat production just as if it was a fat or carbohydrate. This at any rate is the view which has been urged with conspicuous ability by Otto Folin in a series of papers to be subsequently noticed.

Ever since the historical experiment performed by Fick and Wislicenus in their ascent of the Faulhorn, it has been known that nature works in a wonderfully economical way in reference to proteid waste. The increased excretion of nitrogenous waste during muscular work is insignificant as compared with the large and immediate increased output of carbon dioxide. If, therefore, we are to limit our proteid intake to the comparatively small supply necessary to repair our lost tissue, it will be seen at once that we must come down to Chittenden's standard or even below it.

Is it, however, wise for all men to act immediately on Chittenden's advice? This is an all-important question, and one feels some

responsibility in attempting to answer it. We may, however, freely admit that the majority of well-to-do people eat too much proteid. There are not many who limit themselves even to Voit's minimum, and in those who are prone to digestive and uric acid diseases one cannot but feel that improvement in body and mind will be the result of more temperate habits. But any change in the practice of years and of generations should be accomplished gradually, not suddenly. Those who are young and vigorous may remember that the liver is the largest organ we possess, its function is to turn nitrogenous metabolites which may be harmful into urea, which is harmless and easily disposed of, and may gain comfort from the reflection that the organ is adequate in health to deal with large quantities of material.

If all of us were to reduce immediately our diet to the Chittenden level, we might be living perilously near the margin; any unusual strain, such as privation or a severe illness, would then find us without any reserve of nutrient energy, and we should probably suffer more severely in consequence. The poor around us have had *nolens volens* to subsist on a diet very like Chittenden's, but their nutritive condition is not such as to make people who can afford a more liberal table inclined to follow their example. In countries like India, where the vegetarian native population is diluted with the meat-eating white races, it is the former who are more readily attacked by disease and more easily succumb to its effects.

In the modern treatment of consumption, the open air cure is combined with a steady process of overfeeding; in certain cases of nervous breakdown, an important part of the "rest cure" is the providing of abundant and appetising meals. One can hardly doubt that much of the benefit noticeable in both classes is due to the reserve energy provided enabling the body more fully to grapple with the disease.

Now let me take up the work carried out by Otto Folin,[1] to which I have already alluded. He does not appear to have seen that some caution is advisable in accepting Chittenden's conclusions to the full, but he has, nevertheless, published a series of three important papers, full of pregnant suggestions.

The question of What is a normal diet? is intimately bound up with another, and that is, What is a normal urine? The text-book statements of the composition of this fluid are all derived from the examination of the urine of people accustomed to the Voit dietary; but if the diet of the future is to contain only half as much proteid as in the past, the urine of the future will naturally show a nitrogenous output of half of that which is now regarded as normal. In people on such reduced diets, Folin shows that the decrease in urinary

[1] *Amer. J. Physiol.*, 1905, **13**, 45, 66, 117; *Abstr.*, 1905, ii, 183, 268.

nitrogen falls mainly on the urea fraction, and in some cases the urea excreted accounted for only 66 per cent. of the total nitrogen. The other nitrogenous katabolites of the urine alter comparatively little absolutely, but relatively their amount rises; of these, the endogenous purine, and more particularly the creatinine, remain remarkably constant in absolute amount in spite of the great reduction in the proteid ingested.

The laws governing the composition of urine are the effect of more fundamental laws governing proteid-katabolism. Voit's old theory stated that katabolism occurs only in "circulating proteid." The small amount of "living proteid" which dies is dissolved, and so is added to the "circulating proteid." Pflüger's theory, which displaced Voit's, states that all proteid is first transformed into living material before katabolism occurs. The view taken by Folin is that neither of these extreme views is correct, but that nitrogenous katabolism is of two kinds; one is immediate and inconstant; it varies with the food, and leads to the formation of urea and inorganic sulphates, but not of creatinine or "neutral sulphur." The other is smaller in amount, constant in quantity, and is largely represented in the urine by creatinine, "neutral sulphur," and to a less extent by uric acid and ethereal sulphates, and possibly a certain amount of urea. The latter form of metabolism may be termed *tissue* or *endogenous*, whilst the other is *exogenous*. Endogenous metabolism sets a limit to the lowest level of nitrogenous equilibrium attainable; the proteid sufficient to maintain it is indispensable. Whether the amount exogenously metabolised can be entirely dispensed with is at present questionable, but the balance of evidence is believed to show that it can be very largely replaced by non-nitrogenous food; the nitrogen of this part of the proteid is easily split off by hydrolysis without oxidation, and thus a non-nitrogenous residue is left which is available for calorific purposes. The formation of ammonia and amino-acids which occurs so largely in the intestine, owing to tryptic and ereptic activity, is from this point of view regarded as a preliminary means for getting rid of the excess of nitrogen taken in. Any extensive formation from the cleavage products of Voit's circulating proteid to be followed immediately by decomposition into urea is regarded as quite as improbable as the corresponding formation and decomposition of Pflüger's organised protoplasm.

Urea is absent, or nearly so, from the muscles, and its representative, creatine, is eliminated not as urea but as creatinine. The fact that muscular work does not increase proteid katabolism is remarkable if current views of the nature of that katabolism are correct, but it becomes intelligible if proteid katabolism, in so far as its nitrogen is concerned, is independent of the oxidations which give rise to heat, or

to the energy which is converted into work. Whether severe work will have an effect on the endogenous metabolism cannot be shown by investigating urea excretion; determinations of creatinine and neutral sulphur are necessary for a study of that question.

It is hardly necessary to dwell on the importance of work like this, and of the new ideas which arise out of it; other physiologists are entering the field so opened up, and Noël Paton[1] has already had time to publish a paper on some of the points raised. On the whole he agrees with Folin, but certain differences of detail are noted; for instance, in the dog, creatinine excretion is not so constant as in man.[2] He also expresses a doubt whether any hard and fast line can be drawn between endogenous and exogenous proteid metabolism, and urea is probably an end-product in both cases. Some of Folin's results may be explained by variations in the activity of the liver, for it is there that urea-precursors are transformed into that substance. Of all diets, proteid is the most effective in stimulating hepatic activity, as gauged by the amount of bile secreted. Hence, on a diet poor in proteid, the liver may be sluggish, and therefore unable to convert much of the waste nitrogen into urea, whereas on a diet rich in proteid the conversion will be more complete. Exactly similar arguments apply to the sulphur; the amount which is completely oxidised must also depend on hepatic activity.

The current views on the importance of urinary creatinine must obviously be modified if we are to regard it with Folin as the principal measure of endogenous proteid katabolism. Hitherto it has been believed that the greater part of the muscular creatine is ultimately discharged as urea, and that the greater part of the creatinine in the urine came directly from the flesh taken in as food. Several papers have appeared on the subject. Thus, Czernecki[3] performed a research on the question whether guanidine is the parent substance of creatine and creatinine, but his results were not very conclusive. The relation of the methyl groups of lecithin to that of creatinine suggested to W. Koch[4] feeding experiments with lecithin added to a creatine-free diet; he found that the creatinine excreted was increased, but concludes that proteid-katabolism is the main factor involved in supplying most of the nitrogen of the creatinine molecule. Mendel and Closson[5] arrive at the same conclusion. They found the excretion of this substance quite noteworthy in vegetarians and

[1] *J. Physiol.*, 1905, **33**, 1; *Abstr.*, 1905, ii, 734.

[2] W. Koch, on the other hand, states that it is as constant in the dog, and the output per kilogram is nearly the same as in man (*Amer. J. Physiol.*, 1905, **15**, 15).

[3] *Zeit. physiol. Chem.*, 1905, **44**, 294; *Abstr.*, 1905, ii, 467.

[4] *Abstr.*, 1905, ii, 182; also *Amer. J. Physiol.*, 1905, **15**, 15.

[5] *Proc. Amer. Physiol. Soc.*, 1904, xix; *Amer. J. Physiol.*, **13**; *Abstr.*, 1905, ii, 186.

those on a low proteid diet, and in those whose food is free from creatine there is a tendency to parallelism between the total nitrogen output and the excretion of creatinine. There is thus already confirmatory evidence in favour of Folin's views.

Cystinuria.—This is a subject which follows naturally a consideration of normal metabolism, because of all the abnormal variations in intermediary metabolism that which results in the occurrence of cystine in the urine is by far the most interesting.

Loewy and Neuberg [1] opened the discussion by their assertion that the cystine of urinary calculi is not identical with that obtained from proteid decomposition; proteid cystine is α-amino-β-thiolpropionic acid, whereas calculus cystine is β-amino-a-thiolpropionic acid. The special interest of this isomerism arises from the fact that this is one of the rare instances of a β-amino-acid arising during animal metabolism. In a patient who came under their notice, the cystine excreted was unexpectedly found to be proteid cystine. Acting on the supposition that the case was not merely one of anomalous proteid metabolism, but one in which there was a general breakdown of amino-acid metabolism, the urine was searched for other amino-acids, but without success; diamines were also absent.[2] The anomalous nature of the metabolism was, however, shown when amino-acids were administered by the mouth; tyrosine, leucine, and aspartic acid, instead of being broken down in the body, were excreted almost quantitatively in the urine; the same occurred with proteid cystine (given in 6 gram doses), whereas a normal man will burn 8 grams with the formation of sulphates and thiosulphates. On the other hand, the remarkable fact was noticed that calculus cystine was completely burnt with a corresponding increase in sulphates and neutral sulphur. After feeding on lysine, cadaverine (pentamethylenediamine) appeared in the urine, and putrescine (tetramethylenediamine) appeared after the administration of arginine. This is probably due to enzyme action.

The interest of the case is this: if proteids are normally broken up into simple crystalline products, why did not this patient excrete them unchanged, as he did when they were given by the mouth? This tells against the theory of complete proteolytic breakdown in the intestine, although it is quite possible that cystine is specially loosely combined in the proteid molecule.

The remarkable conclusions reached in this work of Loewy and

[1] *Zeit. physiol. Chem.*, 1904, **43**, 338; *Abstr.*, 1905, ii, 103.

[2] The presence of the diamines, putrescine and cadaverine, in the urine of cystinuria is by no means constant. Thus, Bödtker describes two cases in which they were present (*Zeit. physiol. Chem.*, 1905, **45**, 393) and Simon (*ibid.*, 357) one case in which they were absent. Abderhalden and Schittenhelm (*ibid.*, 468) describe a case where both leucine and tyrosine occurred in the urine (*Abstr.*, 1905, ii, 741).

Neuberg had, at any rate, one good effect; it stimulated others to repeat their experiments, and with the result that, within the short space of a few months, nearly every one of their conclusions has been shown to be incorrect. The earliest to enter the lists was Rothera,[1] who was unable to make out any chemical difference between the two forms of cystine, and who also showed that in normal persons both are physiologically broken down and oxidised to sulphate, which appears in the urine quantitatively. He further showed that cholic acid does not diminish the excretion of sulphates, as it might if cystine were converted into taurocholate. The same conclusion is reached by E. Fischer and Suzuki;[2] they could detect no difference between cystine prepared from calculi and that prepared from horse-hair, and they show that Neuberg's contrary result is explicable by admixture with tyrosine. A third set of critics appeared in the persons of O. Folin and Alsberg,[3] and on the chemistry of cystine they hold the same opinion as Rothera and Fischer. The experiments they record in connection with a case of cystinuria do not corroborate the views of Loewy and Neuberg on the nature of the metabolism in this disease. In the early part of the investigation, when their patient was on a Voit diet, the "undetermined nitrogen" in the urine increased. It therefore appeared probable that amino-acids might account for this, and that Loewy and Neuberg's generalisations on the nature of the disease were correct, and that the failure of these observers to discover amino-acids in the urine was only an error of analysis. But this interpretation was shattered by the results obtained when a fat and starch diet was substituted for the one first used, for the undetermined nitrogen remained stationary. If aspartic acid was added to this diet, the nitrogen excreted rose to an amount beyond that which the aspartic acid would account for, and the increase was due to urea, not to undetermined nitrogen; the patient was therefore able to convert the nitrogen of aspartic acid into urea. If pure cystine was added to the diet instead of aspartic acid, the elimination of neutral sulphur was not increased; that is to say, in so far as cystine is absorbed, it is not excreted as such but as ordinary sulphates. There is thus no inability to katabolise normally the usual products of proteolysis, and the cystine which is eliminated is not absorbed as such from the alimentary tract; it comes from other and larger sulphur complexes; it is this and the sulphur from the tissues which the cystinuric person is unable to convert into sulphates.

[1] *J. Physiol.*, 1905, **32**, 175; *Abstr.*, 1905, ii, 267.
[2] *Zeit. physiol. Chem.*, 1905, **45**, 405; *Abstr.*, 1905, ii, 786.
[3] *Amer. J. Physiol.*, 1905, **14**, 54; *Abstr.*, 1905, ii, 544.

Ferments and Co-ferments.

The discovery of such enzymes as arginase, which act on simple crystalline substances, has led to a series of interesting papers. Thus, Schittenhelm [1] concludes that three distinct ferments take part in the transformation of nucleic acid into uric acid, namely, (1) a *nuclease* which hydrolyses the nucleic acid to purine bases; (2) *guanase* and *adenase*, which have deamidising functions, and lead to the conversion of guanine into xanthine and adenine into hypoxanthine respectively; and (3) an *oxidase* which in presence of oxygen converts hypoxanthine into xanthine and xanthine into uric acid. These are widely distributed in different tissues. At the same time there is in the extracts of certain tissues a ferment which has the power of breaking down uric acid, and this is named *uricalase* or the *uricolytic ferment*; among the final decomposition products are glycine and urea. Walter Jones, to whom the discovery of guanase belongs, publishes very similar views.[2]

Emil Fischer and Abderhalden [3] have investigated the action of trypsin on a number of synthetical polypeptides. Some of these are, and others are not, hydrolysed; but it appears too early yet to say what is the cause of the difference.

Passing next to the influence of one ferment on another, a paper by Bayliss and Starling [4] gives a description of experiments which confirm their original contention that enterokinase is a real enzyme; provided sufficient time is given, it is able to convert an unlimited amount of trypsinogen into trypsin, and there is no evidence that trypsin is equivalent to a combination of kinase and trypsinogen.

We have thus firmly established the view originally put forward by Pawloff, that enterokinase is a "ferment of a ferment." This view of the way in which the pancreatic enzyme is activated in the small intestine has now replaced the older theory of Schiff (and supported among others by Herzen and Bellamy), that the spleen forms some substance necessary for the transformation of trypsinogen into trypsin. If any favouring influence is produced by the addition of a splenic extract to pancreatic juice, O. Prym [5] has conclusively shown that it may be simply explained as a result of dilution and bacterial activity, the antiseptics used by the earlier observers mentioned not having been efficient ones.

[1] *Zeit. physiol. Chem.*, 1904, **43**, 228; 1905, **45**, 121, 152, 161; *Abstr.*, 1905, i, 108; ii, 644, 645.

[2] *Zeit. physiol. Chem.*, 1904, **44**, 1; 1905, **45**, 84; *Abstr.*, 1905, ii, 333, 644.

[3] *Sitzungsber. K. Akad. Wiss. Berlin*, 1905, 290; *Abstr.*, 1905, ii, 333.

[4] *J. Physiol.*, 1905, **32**, 129; *Abstr.*, 1905, ii, 273.

[5] *Pflüger's Archiv*, 1905, **107**, 599; *Abstr.*, 1905, ii, 404.

The whole question of co-ferments is, however, in a rather unsettled state just now. As announced in last year's Report, Cohnheim made the striking announcement that the pancreas facilitates the combustion of sugar in the muscles, and it seemed probable that we were to be provided with an intelligible explanation of pancreatic diabetes. The active substance responsible for the action in question is dialysable and not destroyed by boiling, and in these properties resembles the co-ferment of lipase described by Magnus. These expectations have not been fulfilled, for Claus and Embden[1] have been entirely unable to corroborate Cohnheim's results.

It appears that the existence of co-ferments has been hastily assumed in other cases also, and that the simpler explanation of the effect of dilution is much more probable.

The word co-ferment may be of course extended to include the hydrochloric acid of the gastric juice[2] or the calcium which is essential to the activity of rennet and fibrin-ferment, but it is doubtful whether those who coined the word meant to include such inorganic allies of ferments in the expression.

It, however, appears likely that some at any rate of the so-called co-ferments are inorganic; as a rule they are not affected by heat. This is the case in the co-ferment of yeast juice described by Harden and Young.[3] They found that the rate of alcoholic fermentation is greatly increased by the addition of boiled and filtered yeast juice. Buchner and Antoni[4] confirm this observation, and find that the presence of phosphates in the boiled juice accounts for the increase in activity. I understand that Harden and Young, as the result of further work, have arrived at exactly the same conclusion, and that their paper on the subject is already accepted for reading at the Royal Society.

The substance secretin, which Bayliss and Starling found to be the chemical stimulus for pancreatic secretion, may in a still wider sense be considered to come within the category of the co-ferments, and like them its chemical composition is still unknown. The very important discovery that a chemical stimulant is formed within the upper part of the intestine as a result of the action of the gastric acid, and that this material is conveyed in the blood stream to the pancreas, has led naturally to a search for analogous substances in other situations, and

[1] *Beitr. chem. Physiol. Path.*, 1905, **6**, 214, 343; *Abstr.*, 1905, ii, 179, 404.

[2] Compare also the view advanced by Leo (*Zeit. physiol. Chem.*, 1905, **46**, 286; *Abstr.*, 1905, ii, 838) that hydrochloric acid is the effective agent in gastric digestion, and that the part played by pepsin is that of an amboceptor to anchor the acid on to the proteid molecule.

[3] *Proc. Physiol. Soc.*, 1904, i; *J. Physiol.*, **32**; *Abstr.*, 1905, ii, 109.

[4] *Zeit. physiol. Chem.*, 1905, **45**, 136.

Edkins[1] has already adduced some evidence to show that the flow of gastric juice is favoured by the production of a *gastrin*, and that salivary digestion provides a chemical cause for the secretion of the next juice in order. Like secretin, it is not destroyed by boiling. Starling[2] has in the Croonian lectures, which he has entitled "The chemical correlation of the functions of the body," given a concise account of the numerous researches which he and his colleagues have carried out on the chemical messengers which bring about correlation of function between different organs of the body. The general name bestowed on them is *hormone*. Some, like secretin, stimulate increased activity and katabolism, others involve increased assimilation and growth. Under the latter head fall the internal secretions of the thyroid and generative organs. Some preliminary experiments indicate that it is an internal secretion of the fœtus, which leads to the growth of the mammary gland.

Blood Coagulation.—The number of papers on this very controversial subject has not been so great as usual this year. The general question is discussed in a further contribution from the pen of Leo Loeb,[3] mainly as a result of his investigations on the clotting of the blood of invertebrates: it is very similar to that of vertebrate blood. In both, two substances are important, namely, the tissue *coagulins* and substances present in the blood itself. The coagulins are within certain limits specific. The substances in the blood are only specific in so far that those from vertebrate animals have no influence on invertebrate blood. It is probable that the material extracted both from the cellular elements of the blood and from tissues like muscle act directly on the fibrinogen of the blood plasma, but the conditions for their action are different; for instance, the acceleration by calcium salts is more marked with the coagulins than with the material from the blood corpuscles. In certain circumstances, a combination of the two substances is more active than the sum of their individual activities; that this is due to the influence of the coagulin in converting prothrombin into thrombin is only one of several possibilities.

Some discussion as to the meaning of the fibrino-globulin which appears in the coagulation process has taken place between Huiskamp[4] and Heubner.[5] The view taken by the former is that it is present before clotting takes place.

The only other paper worthy of mention is an interesting one by C. J. Martin,[6] who finds that snake venom produces clotting because

[1] *Proc. Roy. Soc.*, 1905, **76** *B*, 376; *Abstr.*, 1905, ii, 730. [2] *Abstr.*, 1905, ii, 735.
[3] *Beitr. chem. Physiol. Path.*, 1905, **6**, 260; *Abstr.*, 1905, ii, 330.
[4] *Zeit. physiol. Chem.*, 1905, **44**, 182; **46**, 273; *Abstr.*, 1905, ii, 499.
[5] *Zeit. physiol. Chem.*, 1905, **45**, 355; *Abstr.*, 1905, ii, 725.
[6] *J. Physiol.*, 1905, **32**, 207; *Abstr.*, 1905, ii, 411.

it contains true fibrin ferment. The small quantity of venom necessary to cause coagulation is remarkable, although it varies in different venoms. There is, further, some specificity in the ferments; the serum of a horse immunised against one venom contains an anti-ferment against the clotting ferment in that venom, but not necessarily in other venoms.

A very simple time relationship was found in investigating the reaction velocity of fibrin ferment, namely, that the amount of ferment and the coagulation time are inversely proportional. As different enzymes are investigated, more and more of them are falling into line in obeying this simple law instead of the law of square roots enunciated by Schutz.[1]

Opsonins.—The consideration of ferments leads us next in logical order to the immunity question, and that subject is rapidly acquiring a literature of its own. I propose to deal only with one part of it, which has risen into special prominence during the foregoing year.

The methods of defence the body possesses against invasion by micro-organisms are numerous, and different bacteria are dealt with in varying ways. In some cases, the bacteria are killed by the bacteriolysins of the blood, but the varieties so dealt with are limited in number. In other cases, the toxins produced by the bacteria are neutralised by antitoxins, and in other cases still the bacteria are directly attacked and devoured by the white corpuscles or phagocytes. In connection with phagocytosis, great differences are noticeable; this has been partly explained by what is called chemotaxis; some bacteria produce chemical substances which act like magnets, attracting the leucocytes to their neighbourhood (*positive chemotaxis*); in other cases, such substances are not produced, or even *negative chemotaxis* may occur, so that the phagocytes are repelled. Recent observations by A. E. Wright, which have resulted in the discovery of *opsonins*, are of great importance in this connection, and make our knowledge of positive chemotaxis more exact. They form a striking illustration of how the leucocytes and body fluids co-operate and how elaborate are the means the body possesses for combating bacterial invasion. The word opsonin is derived from a Greek word which means "to prepare the feast." Bacteria from a pure culture are in many cases distasteful to the leucocytes, but if the bacteria have been previously soaked in serum, especially if that serum has been obtained from the blood of an animal immunised against that special bacterium, then the leucocytes devour them eagerly; in other words, something has been added to the bacterium to make it piquant, and each kind of bacterium apparently requires its own special sauce or opsonin.

[1] Compare Bayliss on "The Kinetics of Tryptic Action" (*Arch. Sci. biol. St. Petersburg*, 1904, **11**, Suppl. 281; *Abstr.*, 1905, ii, 267).

It is in connection with tuberculosis that the opsonin question has been mainly worked out. Without going into the details of the technique, the following is an instance of how practical investigations are carried on. Microscopic films are made of blood which has been previously mixed with an emulsion of tubercle bacilli. The bacilli ingested by, say, fifty leucocytes are then counted, and an average struck. If this is done after admixture with (1) an abnormal serum and (2) a normal serum, the average per leucocyte in the first case divided by that in the second is called the *opsonic index*. In eighty-six healthy people examined by Bulloch,[1] the index was 0·97, the extremes being 0·8 and 1·2. In tuberculosis of the skin (lupus), the average was 0·75 in 150 cases. In 75 per cent. of these, the index was below the lowest normal limit, 0·8 ; in twenty-seven cases it was below 0·5, and in three cases as low as 0·2. It was found that if the index is well below the normal, treatment by the Finsen light is of little or no benefit. The ultra-violet rays have but little penetrative power, and probably exert no potent effect on the bacilli themselves ; its healing properties are due to a reaction set up in the tissues and to the congestion which follows exposure to the rays. If the bacilli are bathed in a fluid rich in opsonin, that is, if the opsonic index is high, they then will fall ready victims to the crowd of leucocytes brought to the spot by the congestion.

In a more general form of tuberculosis (phthisis) it will be sufficient to take one example of the sort of work in progress. Meakin and Wheeler[2] found great variations in the opsonic index even in the same case, especially during the early stages of the disease. It then becomes fairly stationary, and if it is then unity or thereabouts the prognosis is better than when it is low.

Considering the vast amount of work which issues from the Pasteur Institute, it may seem remarkable that opsonins were not discovered earlier. But, as a matter of fact, the favouring effect of the addition of immune serum on the phagocytic action of leucocytes has been known in that institution and chronicled in its *Annales* for some time past. The attitude of mind adopted by Metschnikoff and his disciples has always been to attribute to the leucocyte an overmastering *rôle* in all problems of protective mechanism ; and thus they have considered that the favourable action of the serum is one mainly on the leucocytes, and not so much on the bacilli. Metschnikoff invented the word *stimulin* as the name for the substance in the serum which stimulates the leucocytes to increased phagocytosis. It is probable that both factors must be taken into account. Leishman[3] has made

[1] *Trans. Path. Soc. London*, 1905, **56**, 334 ; *Abstr.*, 1905, ii, 844.
[2] *Brit. Med. J.*, 1905, ii, 1396 ; *Abstr.*, 1905, ii, 845.
[3] *Trans. Path Soc. London*, 1905, **56**, 344 ; *Abstr.*, 1905, ii, 844.

experiments with serum from cases of Malta fever and typhoid fever. This increases the phagocytic activity of the leucocytes on the specific bacilli of these diseases. He concludes that the main effect is a stimulating one on the leucocytes themselves and is not due to the addition of an opsonin to the bacilli. The principal ground for this conclusion is that Wright's hitherto described opsonins are destroyed at a temperature of 60°, but the substances Leishman describes are thermostable and are not affected by exposure to this temperature for fifteen minutes. The possibility, however, still remains that some opsonins are more resistant to heat than others, and even Metschnikoff himself appears inclined to accept this view.

Carbohydrate Metabolism.

The principal question attacked this year has been diabetes, and the principal writer Pflüger; several of his papers are characteristically controversial. He and his colleagues, Schöndorff and Wenzel,[1] examined some hundreds of urines, and conclude that many forms of so-called transitory glycosuria (including those produced by anæsthetics and by surgical operations) do not exist. The contrary conclusion reached by others is attributed to untrustworthy tests for sugar. Most reliance should be placed on the polarimetric test and Worm Müller's modification of the copper reaction.

He has also published two papers[2] on pancreatic diabetes; the first of these is mainly comment on Lüthje's conclusions[3] on the proteid origin of sugar. Pflüger thinks it really originates from fat, and in his second paper explains in a very ingenious way why he still continues to doubt its origin from proteid, even although the dogs he examined were fed exclusively on that substance. Those interested in controversies should read the original papers.

Coming from the same laboratory, one next notes a useful piece of work by K. Grube.[4] He finds the glycogen in the liver is uniformly distributed in the organ; this is by no means an unimportant point when small pieces only are analysed as samples. He also describes a new method of artificial perfusion of the liver which can be applied to the organ *in situ* without any pause occurring after the cessation of the natural circulation. If dextrose, dextrin, or lævulose be added to the defibrinated blood used in perfusion, it is shown conclusively for the first time that the carbohydrate added to the blood becomes less as the glycogen stored in the liver increases.

[1] *Pflüger's Archiv*, 1904, **105**, 121; *Abstr.*, 1905, ii, 44.

[2] *Pflüger's Archiv*, 1904, **106**, 168; *Abstr.*, 1905, ii, 100. *Pflüger's Archiv*, 1905, **108**, 115; *Abstr.*, 1905, ii, 469.

[3] *Pflüger's Archiv*, 1904, **106**, 160; *Abstr.*, 1905, ii, 99.

[4] *Pflüger's Archiv*, 1905, **107**, 483, 490; *Abstr.*, 1905, ii, 334.

Three papers on allied subjects come from America. Lusk and Mandel[1] comment on a case of severe diabetes; the dextrose : nitrogen ratio was 3·65 : 1 on a meat diet. This is the same ratio seen in phloridzin diabetes in dogs, and indicates a rapidly fatal result.

Underhill[2] finds that piperidine and other alkaloids, as well as narcotics, produce hyperglycæmia, and glycosuria, not by specially acting on the pancreas or any other organ, but simply by the dyspnœa they cause by acting on the respiratory centre. Adrenaline diabetes, however, does not fall under this rule.

The number of factors which come into play in the causation of a diabetic condition is still further accentuated by the third paper, which is by J. J. R. Macleod and J. Dolley.[3] Eckhard found that puncture of the medulla oblongata did not cause glycosuria when the splanchnic nerves were cut, and so argued that impulses reached the liver by these nerves. Glycosuria does not follow stimulation of the peripheral end of the cut nerves, but it does occur if the cervical part of the spinal cord is stimulated; hence the somewhat unwarranted supposition had to be adopted that the impulse undergoes some change as it passes through the upper cervical ganglia. In the present research, nicotine was injected to block the impulse at the ganglia; puncture was thus found to produce little or no glycosuria, and glycogen did not disappear from the liver. Stimulation of the central end of the vagus, however, produces glycosuria whether nicotine had been administered or not, and application of nicotine locally to the stellate ganglia during excitation of the vagus renders the urine sugar-free. Still it is unwise to draw important conclusions from these experiments, since the procedure adopted often caused a lowering of blood pressure, and that in itself causes the sugar to disappear.

Gaseous Metabolism.

The respiratory processes are capable of two lines of study, namely, those which are concerned with the phenomena of external respiration and with internal or tissue respiration respectively. I may refer readers who desire to obtain a full account of the external respiratory processes to an article by Christian Bohr in Nagel's *Handbuch der Physiologie* now being issued; it contains among other things a succinct account of the author's own researches, which have extended over many years. A further contribution to this work on the absorption coefficients of blood and blood-plasma for gases has been

[1] *J. Amer. Med. Assoc.*, July, 1904; *Abstr.*, 1905, ii, 187.

[2] *Proc. Amer. Physiol. Soc.*, 1904, xxxvi; *Amer. J. Physiol.*, **13**; *Abstr.*, 1905, ii, 187.

[3] *Proc. Physiol. Soc.*, 1905, lxiii; *J. Physiol.*, **32**; *Abstr.*, 1905, ii, 544.

issued during the year.[1] Leonard Hill and his colleagues[2] have added some more details to their previous work on caisson disease and the gases set free in the body after rapid decompression from high atmospheric pressures.

One of the most important pieces of new work, however, is that carried out by J. S. Haldane, who is well known as an expert in connection with the air in mines. He and Priestley[3] have introduced a new method of obtaining normal alveolar air; it consists in collecting a sample of the expired air at the end of inspiration and another at the end of expiration; the mean of the two gives the composition of alveolar air. This is much simpler than Pflüger's catheterisation method, and has the further advantage that it can be applied to the human subject.

Under constant atmospheric pressure in man, the alveolar air contains a nearly constant percentage of carbon dioxide in the same person. In different individuals, this percentage varies. With varying atmospheric pressures, the percentage varies inversely as the atmospheric pressure, so that the carbon dioxide pressure remains constant. The oxygen pressure, however, varies widely under the same conditions.

These observations and the next to be immediately described furnish the chemical key to the cause of the amount of pulmonary ventilation, and play an important part in conjunction with the respiratory nervous system in the regulation of breathing. For the respiratory centre is not only affected by impulses reaching it by the vagi and other afferent nerves, but it is also very sensitive to any rise in the alveolar carbon dioxide pressure, a rise of 0·2 per cent. being sufficient to double the amount of alveolar ventilation during rest. Changes in the oxygen pressure within wide limits have no such influence; the normal chemical stimulus to respiration is therefore presence of carbon dioxide, and not diminution in oxygen. If these limits are exceeded, as when the oxygen pressure in the inspired air falls below 13 per cent. of an atmosphere, the respiratory centre begins to be excited by want of oxygen, and the alveolar carbon dioxide pressure begins to fall. The changes in the alveolar carbon dioxide pressure are normally proportional to the tension of that gas in the arterial blood, and it is by that channel that the changes in

[1] *Skand. Arch. Physiol.*, 1905, **17**, 104; *Abstr.*, 1905, ii, 729.

[2] *Proc. Physiol. Soc.*, 1905. vi, vii; *J. Physiol.*, **33**; *Abstr.*, 1905, ii, 728.

[3] *J. Physiol.*, 1905, **32**, 225; *Abstr.*, 1905, ii, 400. A second paper by Haldane and Fitzgerald (*J. Physiol.*, 1905, **32**, 486; *Abstr.*, 1905, ii, 539) is mainly statistical. Confirmatory observations on the principal point raised are published by Hill and Ham (*Proc. Physiol. Soc.*, 1905, v; *J. Physiol.*, **33**; *Abstr.*, 1905, ii, 728).

the lung alveoli are transmitted to the respiratory centre. During work, the alveolar carbon dioxide pressure increases slightly, and the pulmonary ventilation is consequently increased. Apnœa is the name given to the cessation of breathing which temporarily follows excessive ventilation of the lungs, as when one takes a number of deep breaths in rapid succession. It depends on a fall of the carbon dioxide pressure in the respiratory centre to below the threshold exciting value, the oxygen pressure at the same time being sufficiently high not to excite the centre. The old idea that apnœa is due to over oxygenation of the blood has been abundantly disproved, and Head and others have gone to the other extreme in assuming that apnœa is purely nervous in origin. Some years ago, Fredericq showed that apnœa can be produced in animals with both vagi cut, and he mooted the idea that fall in the tension of carbon dioxide is its chemical cause. Haldane does not allude to this in his papers, but he nevertheless confirms Fredericq's opinion, and considers that it is unnecessary to assume the existence of a vagus apnœa in man at all under normal conditions.

The whole paper is replete with interest and should be read in full; it contains many other matters which need not be discussed in this report, such as new determinations of the volume of tidal air and of the "respiratory dead space."

Passing now to questions of internal respiration, it is necessary to allude to two researches, one on nerve, the other on the kidney.

The question whether nerves participate in respiratory activity has been answered in the affirmative by Baer, Fröhlich, and others in confirmation of Waller's long-expressed opinion that carbon dioxide is produced during the activity of nerve-fibres. By means of an apparatus called the micro-respirometer, Thunberg[1] has succeeded in actually measuring the respiratory exchange in small objects like nerves. The instrument has also been utilised in measuring the gaseous interchanges in small animals like worms and snails.

The work on the gaseous metabolism of the kidney has been carried out by Barcroft and Brodie.[2] The experiments were made on dogs which had been subjected to evisceration, an operation they survive about eight hours. Diuresis can be produced by the injection of urea, phloridzin, or of salts like sodium sulphate. This is accompanied by a large increase in oxygen absorption. The oxygen absorbed is the best measure of the work of the kidney, for the carbon dioxide formed is not evolved simultaneously; still, over a large number of experiments the volumes of oxygen absorbed and the carbon dioxide excreted are

[1] *Centr. Physiol.*, 1904, **18**, 553; *Abstr.*, 1905, ii, 44. *Skand. Arch. Physiol.*, 1905, **17**, 133; *Abstr.*, 1905, ii, 728.

[2] *J. Physiol.*, 1904, **32**, 18; 1905, **33**, 52; *Abstr.*, 1905, ii, 99, 737.

approximately equal. This suggests, although it does not exactly prove, that the substance of the kidney is broken down in the organ itself. Diuresis is not necessarily accompanied with increase in blood flow, and this is never so great as the acceleration of urine-flow; when it is present, the diuresis outlasts it.

The work of concentration, as calculated from the freezing points of blood and urine, accounts for only a small fraction of the energy transformed by the kidney. In so far as urine of the same freezing point as the serum would represent Ludwig's glomerular filtrate, the experiments yield no support to his theory, for the source of energy for the production of such urine should be the heart and not the kidney, yet it is in these circumstances that the kidney is most active as gauged by the gaseous exchange. In some cases, urine of smaller molecular concentration than the serum was obtained, and this divergence is greatest when the flow of urine is most rapid. The experiments lend little or no support to the theory of reabsorption of water in the kidney tubules, a theory recently revived by the work of Cushny.

In this relation, a series of papers by Loewi[1] and others should be consulted. They consider the main cause of certain forms of diuresis is accelerated blood flow, and in other forms it is a hydræmic condition of the blood.

Adrenaline.

The chemical constitution of adrenaline and the synthesis of certain substances allied to it were fully entered into in my report of last year. It will be sufficient to add now, that the physiological action of these and other synthetical substances has been fully worked out by Dakin,[2] and later by Loewi and Hans Meyer.[3] The formula given for Dakin's final product is that which Jowett assigns to adrenaline; but there are certain differences between the new base and adrenaline, for instance, the former is optically inactive. Its salts, however, show all the reactions of those of adrenaline, and its physiological activity is as great; less than a millionth of a gram will raise the blood pressure.

The intermediate ketone (Friedmann's adrenalone) is not much more powerful physiologically than the chloroacetylcatechol from which it is prepared.

Inorganic Salts.

The number of papers published on inorganic salts is numerous; most of them relate to questions of physical chemistry, and seek to explain vital phenomena such as rhythm and nerve activity on an

[1] *Arch. exp. Path. Pharm.*, 1905, **53**, 15, 33, 49; *Abstr.*, 1905, ii, 739.
[2] *Proc. Physiol. Soc.*, 1905, xxxiv; *J. Physiol.*, **32**; *Abstr.*, 1905, ii, 410.
[3] *Arch. exp. Path. Pharm.*, 1905, **53**, 213; *Abstr.*, 1905, ii, 846.

electrolytic basis. Researches of this kind leave the subjects treated, however, in a hypothetical state, and for this reason, as well as for want of space, my allusions to these papers must be more of the nature of a catalogue than is wholly desirable. The following are a selection of the most important.

Overton[1] publishes a very important series of experiments with various salts on the frog's sartorius. Among the many points raised it will be sufficient to mention one, namely, that the harmful action of potassium ions is like that caused by curare. I mention this one because it is also taken up by Locke,[2] who points out certain differences between the action of the two substances.

Benedict[3] records experiments on heart strips, and the results obtained do not bear out Howell's views. The principal main conclusion drawn is that it is the anion, not the cation, which stimulates. One must, however, point out that the practice of performing experiments on strips of the heart, so common in America, although it leads to results of interest, is not well calculated to discover the cause of the cardiac rhythm in the intact organ during life.

J. Loeb[4] has continued his experiments on the antagonism of salts in reference to the growth of fundulus eggs, but W. A. Osborne[5] points out that the so-called antitoxic action of bivalent cations is susceptible of a simpler explanation than that given by Loeb.

A. B. Macallum[6] is still prosecuting his useful work on the microchemical detection of inorganic elements. His cobalt nitrite reagent for potassium shows that element to be present in cell protoplasm, but more abundantly in intercellular material; in striped muscle, it is limited to the dark bands, and in pancreatic cells to the granular zone. It is absent from nerve cells and from the nuclei of all cells. In nerve fibres, it occurs in curious patches external to the axis cylinder, especially at the nodes.

The second paper quoted deals with the well-known reduction stain with silver nitrate so much used in histology. The conclusion reached is that this is not due to a reduction of a silver-proteid compound, but to inorganic chlorides. Intercellular material is specially rich in chlorides, and the reaction may be employed to determine the distribution of chlorides in histological specimens. The normal nuclei of animal and vegetable cells contain no chlorides at all.

[1] *Pflüger's Archiv*, 1904, **105**, 176; *Abstr.*, 1905, ii, 46.
[2] *Proc. Physiol. Soc.*, 1904—1905, xxii; *J. Physiol.*, **32**; *Abstr.*, 1905, ii, 270.
[3] *Amer. J. Physiol.*, 1905, **13**, 192; *Abstr.*, 1905, ii, 330.
[4] *Pflüger's Archiv*, 1905, **107**, 252; *Abstr.*, 1905, ii, 400.
[5] *Proc. Physiol. Soc.*, 1905, x; *J. Physiol.*, **33**; *Abstr.*, 1905, ii, 746.
[6] *J. Physiol.*, 1905, **32**, 95; *Abstr.*, 1905, ii, 270. *Proc. Roy. Soc.*, 1905, **76** *B*, 217; *Abstr.*, 1905, ii, 736.

J. S. Macdonald[1] amplifies one of Macallum's conclusions. His work was directed to obtaining a physical explanation of the electrical changes which occur in nerves. He found by the use of certain stains that granules which are deposited at the seat of an injury are stainable by "neutral red." The colour differs according to varying conditions; for instance, a cooled fibre is alkaline, a warmed one acid. Attempts to alter the reaction by activity failed. The granules are probably stained coagula of proteid, and the appearances are similar to those described by Macallum in his potassium reaction. By Macallum's method, potassium salts may be detected wherever an injury occurs, and the patchy appearance Macallum describes is attributed to injury of the axis cylinder at those spots. Not only are potassium salts liberated from the axis cylinder, but the amount found leads to a salt solution of great concentration at the injured spot, as measured by the extraordinarily concentrated solutions necessary to balance the injury current so produced.

The Pathology of Cancer.

This is the only subject of a pathological nature upon which I will permit myself to dwell. It is a question fraught with interest to all, and at numerous centres research and money are being expended with no unwilling hands in attempts to grapple with this scourge of humanity. It must be confessed that up to the present the disease has baffled all attempts to unravel its causes, and hope for the healing of sufferers seems as far off as ever. The surgeon's knife, if applied at a sufficiently early stage, is the only remedy, but that cannot always reach deep and hidden structures, and if the tumour is accessible, it is a mere matter of chance whether every particle is even then removed.

It may be that some of those who have subscribed of their wealth toward Cancer Research may be disappointed at the paucity of the results obtained after so many years of labour. But there will be others who realise that money cannot buy everything, and will sympathise with failure, especially if they have any idea of the difficulties which beset biological and pathological researches in general, and those relating to cancer in particular.

If a number of eager and capable investigators were set to find out the cause of an infectious disease, one cannot doubt that the search, although it might be difficult, would be attended with ultimate success, for such workers would have the previous researches of

[1] *Proc. Physiol. Soc.*, 1905, xxxvii; *J. Physiol.*, **32**; *Abstr.*, 1905, ii, 405.

others to guide them in the investigation of other diseases of the same order, and the micro-organism, either animal or vegetable, would thus be brought to light.

But malignant disease appears to be one *sui generis*. It does not run on the same lines as any other pathological condition, and all attempts to work at it by the older methods have yielded negative results. One is therefore groping in the dark looking for a new and invisible path along which to progress. One fact which the research of recent years has demonstrated is that the various bacteria and protozoa from time to time described as the active agents in cancer are merely accidental concomitants, or the erroneous interpretation of microscopic appearances. The parasitic theory of cancer-causation is killed, and serum treatment on immunity lines has so far failed.

A special stumbling-block is met with at the outset in the difficulty, and often impossibility, of transmitting the disease to animals, or of producing it in them. Hence at once the field of experimentation is limited.

In addition to this negative conclusion, there is at any rate one positive finding of some interest, and it may ultimately be shown to be more important than it appears to be at present. Such discoveries at any rate encourage further work, and show that the problem may not be so hopeless as it seems at first. The discovery in question was not made by pathologists or even by medical men, but by those who devote their lives to the calmer atmosphere of biology. Farmer and Moore showed that the actively multiplying units of malignant growths go through the process of cell-division in an unusual manner, or, to use the technical expression, the mitosis of their nuclei is heterotype. The same unusual behaviour of the cell nuclei is seen in certain stages of the formation of the generative elements. It therefore appears that the cancer cell is either a cell of embryonic type or that it has reverted to embryonic habits.[1] The cause of such reversion and the explanation why such reversion should generate a malignant disease is still to be discovered.

We now come to see what chemistry has done to help in the matter. Many years ago, the statement was made that in cancer of the stomach the hydrochloric acid of the gastric juice disappeared, and this fact was urged as a useful means of diagnosis between malignant disease and a simple ulcer. Although the absolute statement has been doubted from time to time, there is no longer any hesitation in accepting it as proved that, if the acid does not entirely disappear, it

[1] The most recent paper on the subject is by Farmer, Moore, and Walker (*Trans. Path. Soc., London*, 1905, **56**, 377), and deals especially with the behaviour of leucocytes in malignant growths.

is at any rate much reduced in quantity. B. Moore[1] has further shown that this is not merely a local effect on the stomach wall, but the same reduction or abolition of the gastric acid occurs in cancer of other organs, even although the stomach itself is not affected, and that it is due to diminished concentration of hydrogen ions in the blood plasma. It is, however, extremely doubtful whether a maintenance of the normal concentration would counteract the effects of cancer, but that, of course, cannot be asserted until the experiment is tried, and at present there is no means available for trying it, for the administration of acid below the limit of acid-intoxication merely calls forth protective ammonia production from the oxidation of proteids.

Another line of research consists in the chemical examination of the tumours themselves. Carl Neuberg[2] draws attention to certain abnormal fermentative occurrences in the growths, and believes that such influence as radium possesses on carcinomatous tissue is by altering the ferment actions. By autolysis of liver-cancer, free pentose makes its appearance, whereas in normal liver tissue this does not occur. The high percentage of pentose in cancerous tissue is regarded as being due to its richness in nuclei.

S. P. Beebe has published a series of papers on the composition of tumours. The first[3] relates to their inorganic constituents, but the experiments are confessedly too small in number for conclusions to be drawn regarding the differences between benign and malignant specimens. The next[4] relates to proteids, and special search was made for nucleo-histon; this proteid does not appear to be a common constituent of tumours unless they occur in connection with lymphatic tissue of which nucleo-histon is a normal constituent. The third, written in conjunction with Shaffer,[5] deals with the pentose question raised by Neuberg. In cancer of the breast, they found the amount of pentose higher than in normal breast tissue, and it is sometimes extremely high in cases of chronic scirrhus, where nuclear proliferation is not a marked feature, so that Neuberg's suggestion of a nuclear origin is hardly confirmed.

In the tumours of the liver examined, the amount of pentose did not markedly differ from that found in the normal organ; the pentose content of normal tissues varies considerably; they conclude that many more observations are needed before any theory on the relation of cancer and pentose can be considered satisfactory.

[1] *Proc. Roy. Soc.*, 1905, **76** *B*, 138; *Abstr.*, 1905, ii, 741.
[2] *Berlin klin. Woch.*, 1905, 118; *Abstr.*, 1905, ii, 338.
[3] *Amer. J. Physiol.*, 1904, **12**, 167; *Abstr.*, 1904, ii, 755.
[4] *Amer. J. Physiol.*, 1905, **13**, 341; *Abstr.*, 1905, ii, 408.
[5] *Amer. J. Physiol.*, 1905, **14**, 231; *Abstr.*, 1905, ii, 742.

Many more observations of all kinds are equally necessary before our knowledge of cancer is sufficient to enable us to formulate any workable hypothesis of its cause, and still more to effect its cure. The fragments of research just described may in the future form portions of the picture; as yet even the outline is not discernible, but there can be little doubt that chemists will play their part with others in the final composition. W. D. HALLIBURTON.

AGRICULTURAL CHEMISTRY AND VEGETABLE PHYSIOLOGY.

When summing up, a year ago, the record of "Progress in agricultural chemistry in 1904," it was pointed out that there was no one outstanding feature which marked the year's work and which could be designated as a great discovery in the sense that this term is applied to that which is at once startling and far-reaching in its results. The year 1905 can, however, claim to be associated with a discovery which, whatever be the practical outcome in its application to agriculture, is of a most highly interesting nature, and which marks the working out of ideas which have existed ever since Cavendish, in 1784, showed that the oxygen and the nitrogen of the atmosphere could be made to unite under the influence of the electric discharge. Many have been the efforts to bring this discovery into practical working and to lay the atmosphere, with its unlimited store of nitrogen, under contribution to agriculture, the main needs of which, as shown by Lawes and Gilbert, consist in the adequate supply of nitrogen in a form in which it can be taken up by the living plant. This has now been effected by the discovery of a method of producing calcium nitrate from the nitrogen of atmospheric air, and, so far as agricultural chemistry is concerned, it forms the most striking item in the year's progress.

As in 1904, interest has turned mainly on the "nitrogen question," and this not alone in the direction just indicated, but in other ways whereby either nitrogen-containing materials may be brought to the service of the plant, or where the bacteriological conditions may be so arranged that the plant may itself be able to utilise the nitrogen of the air as it circulates in the soil. The researches in this direction have centred in the further examination of the two principal matters mentioned in last year's report, namely, cyanamide and inoculating materials known under the general term "nitragin." Within the last few weeks the statement has also been put forward of a further discovery regarding the way in which, not leguminous plants only, but cereal and other agricultural crops, make use of atmospheric nitrogen, but of this the details are not yet to hand.

In further pursuit of inquiry on the utilisation, by cereals, of

nitrogen stored up by leguminous crops, experiments on green-manuring have been continued. These investigations, conducted in the one case in the field and in the other by pot-culture methods, have led to the noting of differences which raise considerable question as to how far the one plan of inquiry is comparable with the other.

Investigation in regard to soils has hardly turned in any fresh direction, but further useful work has been done on the solubility of soil-constituents in different solvents and on the oxidation of soil. The subject of lime in soils and the influence which lime exercises has received much attention, alike as regards its occurrence in relation to magnesia and other soil-constituents, and in reference to its rate of removal from the soil under known conditions.

Further work has been done on the influence of small applications of the less common materials which may be concerned with plant nutrition, these embracing such substances as manganese, zinc, iron, chlorine, &c. In plant physiology, the most important contributions have been those of Horace T. Brown and F. Escombe on the physiological processes which go on in the green leaves of plants. The preponderating influence of "variety" in cultivated plants of the farm has been emphasised by field experiments carried out in the case of wheat by A. D. Hall, and by T. B. Wood and S. H. Collins with root crops.

Further investigations by E. J. Russell into the losses which farm-yard manure undergoes in making and storing have gone to prove the accuracy of former work on this subject.

These several points will be dealt with in detail further on.

Among matters of general interest mention may be made of the continued activity of the Rothamsted Experimental Station, and of the issue, by the Director, A. D. Hall, of *The Book of the Rothamsted Experiments*,[1] in which is given, in a very clear and, at the same time, popular way, a summary of the work of this renowned experimental station since its inception, in 1843, by Lawes and Gilbert. The main features of the work are admirably summarised and brought up to date, while their bearing on agricultural practice of the present day is set out in a comprehensive and definite manner.

The visit of the British Association to South Africa furnished an occasion for the introduction and discussion of the various problems exercising the minds of workers in agricultural science at the present time, and specially in relation to that great country and its agricultural possibilities.

From India one hears with interest of the expansion of the work of agricultural inquiry, this being now fostered both by Government Departments and private individuals, as well as by commercial industries. The Government of India has decided on the establishment

[1] *The Book of the Rothamsted Experiments*, by A. D. Hall (John Murray), 1905.

at Pusa, in Lower Bengal, of an Agricultural Research Station and Laboratory, connected with which will be an experimental farm, 800 acres in extent, and also an Agricultural College. This has been the outcome of a munificent donation by Mr. Henry Phipps of £20,000, to which a further sum of £10,000 has since been added by Mr. Phipps. Further, the Indian Tea Association have resolved to institute at Heeleaka, near Moriani, Assam, an experimental station where the various problems connected with the culture of the tea plant can be investigated. Both these spheres of inquiry, begun, as they have been, under favourable auspices and with capable men to carry them out, bid fair to be productive of much benefit and to call for more workers in the near future.

While these advances have to be recorded, it is a matter for regret to note the cessation of the Guinness Research Laboratory, the record of the work conducted at which formed so prominent a feature in the review of last year's progress. It was confidently expected that from this Institution would proceed a regular series of results of investigation of the highest importance, a hope which was fostered by the issue, in 1904, of the first part of the transactions, under Dr. Horace Brown's direction.

From the continent has to be recorded the retirement, after a service of more than forty years in this position, of Dr. F. Nobbe, of Tharand, from the editorship of the journal *Die Landwirtschaftlichen Versuchs-Stationen*, his place being now taken by Dr. O. Kellner, of Möckern.

On May 18th, 1905, died Dr. A. Hilger, of Munich, who, since 1878, had been editor of the *Jahresbericht über Agrikultur-Chemie*. This, happily, is the only great loss by death to record in agricultural science throughout the year.

The Nitrogen Question.

(a) *Inoculation of Leguminous Crops.*

This operation, as being the direction in which the problem of the utilisation of atmospheric nitrogen has in more recent years been mainly attacked, will be dealt with first. In last year's report mention was made of the improved methods, by Hiltner, of Munich, on the one hand, and by G. Moore, of the U.S.A. Department of Agriculture, on the other, of preparing materials for the purpose of inoculating leguminous crops so as to enable them to take up and utilise the free nitrogen of the atmosphere. The year 1905 has seen the first trial, alike on the Continent, in America, and in our own country, of these preparations, and, although the inquiry is far from complete, yet as the outcome of the year's experience, some general conclusions may be

drawn as to the likelihood of either method of inoculation becoming a recognised part of agricultural practice.

In Great Britain, the Board of Agriculture interested itself largely in the inquiry, and, having obtained supplies of the inoculating material direct from Germany and America, proceeded to distribute these to various agricultural colleges where experimental work was conducted and also to the Woburn Experimental Station of the Royal Agricultural Society of England. Suggestions were also made as to the lines on which the inquiry might be conducted. In all, thirteen different institutions took part in the work, and the results are shortly to be published. Where the inquiry was carried out in its entirety, the experiments were conducted in three different ways : (*a*) with sterilised soil ; (*b*) with ordinary soil by pot-culture methods ; (*c*) under ordinary farming conditions in the field. In some instances there was an extension of the scope by the use of sterilised sand as well as of sterilised soil. The general outcome of the work was that while in a certain number of cases there was some indication of benefit having been derived from the inoculation methods, there were many more instances in which either negative or else unfavourable results were obtained. The element of consistency between the apparently successful results was missing, and where, for example, at one station barley seemed to be benefited, peas were not, while at another station peas were improved, but beans not. At the Woburn Experimental Station, the only instance of benefit derived was in the case of the *Melilotus* crop, with the American inoculation, the other trials having produced little more than negative results, although carried out on sterilised soil, on unsterilised soil which had not borne a leguminous crop for twenty years, and on an ordinary fertile soil. In one series, conducted at the Midland Institute, Kingston, near Derby, successful results were obtained when sterilised sand was used, but these were not reproduced when sterilised or when ordinary soil was employed. Of the experiments on farm soil under ordinary conditions, it must be said that with one or two exceptions they failed to show any beneficial outcome from the treatment. It may, of course, be argued that these soils were, through previous growth of leguminous crops, already supplied with the organisms which the inoculation was intended to provide, and hence had no further need for these. It is only fair, also, to mention that in several cases the inoculating materials had been obtained some time previous to their being actually used, and so they might have suffered from not being as fresh as was desirable. As between the German preparations of Hiltner and the American ones of Moore, what there was to choose was in favour of the German method.

Altogether, as the outcome of the inquiry in this country during 1905, it cannot be held that there is anything to encourage the belief

that inoculation for leguminous crops has reached a stage at which it can be recommended for adoption in general agricultural practice.

Turning to experiments conducted elsewhere, F. T. Shutt[1] reports from Canada the results of a number of experiments carried out in various parts of the Dominion with both the German and the American preparations. The German preparations, tried over a series of years, gave no clear evidence of benefit accruing, and the vitality of the cultures was found to be very uncertain unless these were used quite shortly after their preparation. More recently, the new American cultures for red clover and alfalfa were employed, but did not show clear benefit in any case. Shutt points out that, as regards, at least, Ontario and the Eastern Provinces of Canada, the necessity for inoculation is not nearly so great as was at one time thought, but that, where clover has been found to fail, this is to be attributed to deficiency or excess of moisture, or to unsuitable mechanical condition of soil, rather than to the absence of nitrogen-assimilating germs. He notes that in an extended agricultural tour he found the presence of root nodules on clover to be universal. A. D. Hall[2] indicates that much turns on the virulence possessed by the sub-cultures used for inoculation, and that this may be greatly modified by growing on particular media, by a high temperature, or even by long-continued growth under laboratory conditions. Inoculation is much more likely to be required where new land is being brought under cultivation than where leguminous crops have been previously grown. The question of the successful growing of lucerne on South African soils calls for consideration in this connection. J. Golding[3] directs attention to the necessity of realising, as far as possible, the conditions under which the organism works in the nodule, and to the difficulty of reproducing under artificial conditions the actual process of fixation as it occurs in the nodule. His observations have led him to regard as very desirable the removal of the soluble products of growth during the assimilation process, so that the conditions obtained in nature can be produced. This he has effected by the use of a porous Chamberland filter-candle fixed in the culture vessel, and has found a more favourable assimilation of nitrogen to result through the removal of the soluble products of growth, a function probably fulfilled under natural conditions by the host-plant.

Whether longer experience may lead to the production of inoculating materials practically useful in agriculture still remains an open question, but it would seem at least fairly certain that, up to the

[1] Canada Department of Agriculture, *Annual Report on Experimental Farms*, Ottawa, 1905, p. 165.

[2] "Recent Developments in Agricultural Science," *Brit. Assoc. Reports*, Section *B*, S. Africa, 1905.

[3] *J. Agric. Science*, **1**, Jan., 1905, p. 59.

present time, there has been something in the method of preparation of the cultures which has resulted in the partial or complete destruction of their efficacy, and there is certainly not as yet any clear evidence to justify a recommendation of their use in agricultural practice.

(b) *Cyanamide.*

In last year's report, an account was given of the manufacture of calcium cyanamide and its sale under the name "Kalkstickstoff." Further trials with it were made in 1905. At Rothamsted, A. D. Hall[1] tried it in comparison with ammonium sulphate for mangels, swedes, and mustard, but the results were of indefinite character, and the most that could be said was there was nothing to indicate that cyanamide was, unit for unit of nitrogen, worth more than ammonium sulphate.

Cyanamide cannot be used as a top-dressing, as loss of ammonia then takes place, nor can it be mixed with superphosphate or similar manures, since the mixture gets very hot. W. Zielstorff,[2] in conducting pot-experiments with mustard, found that when the cyanamide was sown with the seed its value as compared with sodium nitrate was 88·4 : 100, whereas if applied ten days previous to the sowing of the seed the value increased to 92·8 per cent. Zielstorff also ascertained that cyanamide left practically no residue for a second crop to benefit by.

E. Haselhoff[3] showed that germination was injuriously affected if calcium cyanamide were present in the proportion of 0·025 gram to 100 grams of soil, but that harm might be avoided by application of the cyanamide well in advance of sowing of the seed.

C. von Seelhorst and A. Müther,[4] in comparing calcium cyanamide with ammonium sulphate, found that in the case of a sandy loam the manurial value was about equal in the two cases, but that when used in sand-cultures, calcium cyanamide was injurious to vegetation, probably because of the presence of calcium carbide.

F. Löhnis[5] experimented with several different micro-organisms in order to see what effect they would have on calcium cyanamide. He found that *Bacterium Kirchneri, B. lipsiense, B. megatherium, B. vulgare var. Zopfi,* and others liberated ammonia from cyanamide at the ordinary temperature and that aëration took no essential part in the process.

R. Perotti,[6] having previously shown that for calcium cyanamide to act

[1] *J. Agric. Science*, **1**, Jan., 1905, p. 147.
[2] *Bied. Centr.*, 1905, **34**, 217.
[3] *Jahrb. Landw. Versuchs-Stat.*, Marburg, 1904–5.
[4] *J. Landw.*, 1905, **53**, 329.
[5] *Centr. Bakt. Par.*, 1905, [ii], **14**, 309.
[6] *Chem. Centr.*, 1905, **2**, 1507.

as a fertiliser it must undergo decomposition in the soil, experimented with it in conjunction with peat, and he then found that hydrolytic decomposition took place more rapidly than in aqueous solution, and that there was no appreciable loss of nitrogen. From this he was led to suggest the use of peat along with calcium cyanamide for the more rapid decomposition of the latter, and to advise the use of peat with fertilisers containing calcium cyanamide.

In general, as regards the use of calcium cyanamide, it may be said that the evidence so far points to it being beneficial, although hardly to the same extent as ammonium sulphate, whilst its practical success in the future must depend entirely on the cost price at which it can be produced as compared with ammonium sulphate supplying an equal amount of ammonia.

(c) *Calcium Nitrate.*

Undoubtedly the subject which has given rise, during the year 1905, to the greatest interest so far as agricultural science is concerned, is that of the discovery of a new method of utilising atmospheric nitrogen. This has been effected by Birkeland and Eyde's process, which has been fully described by O. N. Witt.[1] Briefly, this consists in the production of nitric acid through the combination of the elements of the air under the influence of electricity generated in a furnace of great intensity. The nitric acid is then transformed into calcium nitrate by passing it into lime water, and subsequent manipulations result in the production of a salt which can be used directly on the soil as a fertiliser. That small quantities of nitric acid are formed under the influence of atmospheric electricity has long been known, but these amounts are far too small to be of any agricultural importance. In face of the conclusions arrived at by Lawes, Gilbert, and Pugh, that plants are unable to avail themselves of the uncombined nitrogen of the air, and that it is in the form of nitrates that they take up nitrogen, recourse has been had to the use of sodium nitrate and other nitrate-yielding materials and to the cheaper production of these. If the atmosphere could be made to produce these nitrates in sufficiency it is clear that an unlimited source of supply would be ready at hand. The present discovery, which may be described as Cavendish's experiment on a larger scale, and carried out under more favourable conditions as regards electrical energy, has been achieved by Birkeland and Eyde at Notodden, Norway, where water power of enormous extent is available. Atmospheric air is led into a specially constructed electric furnace, in which it is heated to a very high temperature under the influence of an electric arc spread out into disc-like shape by the action of powerful electro-magnets; oxides of nitrogen are formed from the air

[1] *Chem. Ind.*, 1905, **28**, 699.

thus introduced, and these are conveyed into a series of towers in which they are condensed in water and the liquors allowed to concentrate, the weak acid being used over and over again in the towers until a strength of about 50 per cent. is attained. The gases are then led into milk of lime, and after that over dry lime, whereby calcium nitrite is mainly formed. By treatment with nitric acid, a calcium nitrate containing about 13·2 per cent. of nitrogen is obtained as a salt, which can then be employed direct as a fertiliser of the land. One objection to the product, namely, its hygroscopic nature, has been overcome by R. Messel, who, by mixing the calcium nitrate so obtained with calcium oxide, or with calcium sulphate, and calcining the mixture, has obtained a basic calcium nitrate, ($2CaO,N_2O_5$), which is non-hygroscopic and which, when powdered, can be readily applied to the land. It would, of course, be possible to obtain sodium nitrate in place of calcium nitrate by using sodium carbonate instead of lime, but the calcium nitrate is preferred both on account of the cheapness of the lime and because of the agricultural benefit which the use of lime will in many cases confer, more particularly when soils are deficient in this necessary constituent.

Practical trials have been made already with the calcium nitrate, and these would seem to indicate that it is just as effective as sodium nitrate, supplying the same amount of nitrogen. Indeed, there is no reason why this should not be the case. T. Schlœsing [1] carried out pot-culture experiments with maize, in which the use of calcium nitrate and calcium nitrite was compared with that of sodium nitrate and nitrite respectively, and the calcium salts were shown to be equally as efficacious as the sodium ones. Also E. S. Bellenoux [2] experimented with calcium nitrate and sodium nitrate in the field on crops of potato and sugar beet, and found that the calcium salt gave in each case the better result. The calcium nitrate in these experiments, however, had not been obtained by the electric process above described, but from sodium nitrate and calcium chloride, whereas in T. Schlœsing's experiments the electrically-produced salts were used.

If calcium nitrate can be obtained by the electric process at a price at which, as regards its percentage of nitrogen, it can compare favourably with sodium nitrate, it is clear that enormous benefits are at hand so far as agriculture is concerned. So far we have but little information to guide us as to what the cost of manufacture is, and it is still early, therefore, to build great hopes on the prospects. The provision of water-supply adequate for the production of electric power at a cheap rate is evidently the determining factor, but, from a scientific point of view, the discovery of this new process constitutes one of the most important advances of the century. It is to be

[1] *Compt. rend.*, 1905, **141**, 745, 746. [2] *Ibid.*, **140**, 1190.

hoped, however, that in the case of an undertaking possessing such far-reaching possibilities nothing will be allowed to interfere with its development on strictly scientific lines, and with its furtherance for the benefit of agriculture.

(d) *Direct Utilisation of Nitrogen by Plants.*

Following on the foregoing development, there comes, just at the close of 1905, the announcement of a further discovery by T. Jamieson, of Aberdeen, which is, in effect, that he has found that not leguminous plants only, but cereals, grasses, and plants in general have the power, by the medium of certain structures on their leaves and leaf-stalks, of taking in and utilising directly the nitrogen of the atmosphere. This process is said to be only exercised by the leaves and leaf-stalks in their youngest state. Up to the present the details of the work are not to hand, and therefore it is impossible to criticise them or to do much more than merely record the facts as stated. At the same time, we can hardly be prepared, despite recent subversions of some of our views based on the earlier work of Lawes and Gilbert, to accept off-hand a statement so contrary to the conclusions of past experience, or to think that the existence and functions of these special organs have hitherto escaped the notice of plant physiologists.

(e) *Fixation of Nitrogen without Symbiosis.*

G. S. Fraps,[1] in giving the result of experiments on soil bacteria, mentions that free nitrogen is assimilated by them without symbiosis and that the greatest activity occurs in an alkaline solution containing glucose, potassium phosphate, sodium chloride, magnesium sulphate, and ferric chloride, calcium carbonate being also present. Nearly all the nitrogen was fixed in the first week of the experiment, and a small amount only in the second week. The replacing of glucose by starch did not increase assimilation of nitrogen, and the activity was reduced when magnesium sulphate was omitted. E. B. Voorhees and J. G. Lipman[2] concluded from experiments conducted with cow-peas that non-symbiotic fixation of nitrogen was most active in open soils containing fairly large amounts of organic matter but having only a low percentage of nitrogen. The soils gained nitrogen during the growth of the cow-peas, and fixation of nitrogen was believed to continue after their removal and during the growth of subsequent crops of millet. When organic matter was present in the soils, nitrogen-fixation went on actively, but if large amounts of a leguminous crop were incorporated with the soil no gain of nitrogen was shown.

[1] *Agric. Expt. Stat. N.C., Report of Chemist*, 1902–3, p. 40.
[2] *J. Amer. Chem. Soc.*, 1905, **27**, 556.

The question as to how the organism *Azotobacter chroococcum*, discovered by Beyerinck, effects its work of nitrogen-fixation is still surrounded with uncertainty, Beyerinck himself now inclining to attribute its power to the presence of certain other organisms living practically in symbiosis with it. It is clear, however, that this organism, which exists freely in most cultivated soils, can, in a medium containing phosphate and other nutrient salts, but no nitrogen, fix nitrogen actively if 1 or 2 per cent. of a carbohydrate be present. Thus, A. D. Hall[1] found, with a Rothamsted soil, that, when mannitol was used, for every gram of this compound 19 milligrams of nitrogen were fixed. In considering where the supply of carbohydrate is to come from, he takes the case of land allowed to run wild and compares it with arable land under regular cultivation but unmanured. The latter has shown practically no gain of nitrogen and hence absence of nitrogen-fixation, but the land allowed to run wild has, by the annual return of carbohydrate matter to the soil, supplied what the *Azotobacter* requires, and the increase of nitrogen has, in consequence, been very large, and this although leguminous plants were found by botanical examination to be practically absent. He concludes that the fixation of nitrogen must be a process depending on the oxidation of the carbohydrate matter, this supplying the needed energy. In this connection, it may be pointed out that Henry[2] has shown that the fallen leaves of forest trees bring about fixation of nitrogen during their decay. The activity of *Azotobacter* has further been shown by A. Koch to be dependent on the presence of calcium carbonate in the soil, and this has been confirmed at Rothamsted, the development of the organism being found to be much more feeble in soils which have not been chalked than in those thus treated.

Keutner[3] has found that *Azotobacter chroococcum* and *Clostridium Pasteurianum* are widely distributed in sea water; they are present on algæ and on plancton organisms, and *Azotobacter* will still show the power of fixing nitrogen in an 8 per cent. solution of sodium chloride.

Soil Organisms.

G. S. Fraps[4] distinguishes four groups of organisms in soil, three of which successively convert organic nitrogen into ammonia salts, nitrites, and nitrates, and a fourth which produces nitrites or nitrates directly from organic nitrogen. The nitrifying of an organic nitrogenous material like cotton-seed meal would, according to Fraps, be carried out

[1] *Brit. Assoc. Report*, Section B, S. Africa, 1905, and *J. Agric. Science*, 1, May, 1905, p. 241.

[2] *Bied. Centr.*, 1904, **33**, 795.

[3] *Chem. Centr.*, 1905, i, 395.

[4] *Agric. Exp. Stat. N.C., Report of Chemist*, 1902-3, 9.

by a different group of organisms to that which nitrifies ammonium sulphate. He found that ammonium sulphate was nitrified more quickly than either ammonium phosphate or chloride.

A. Stutzer and W. Rothe [1] carried out experiments with eight varieties of soil micro-organisms, and these showed that ammonium sulphate was a better food than sodium nitrate, also that the presence of calcium carbonate and ammonia favoured the production of organic nitrogen compounds by various soil microbes. F. Löhnis [2] came to the same conclusion, regarding nitrogen in the form of ammonium salts as being more readily assimilable than nitrates, and he found that various nitrogen-assimilating bacteria, such as *Bacillus radicicola* and *B. radiobacter*, could assimilate nitrates, while *B. agreste* did not fix nitrogen, but assimilated nitrates vigorously. *B. fluorescens*, on the other hand, caused nitrates to disappear, and mainly by denitrification. Löhnis [3] also came to the conclusion that denitrification in soils can be but inconsiderable owing to the amount of air present, and that nitrification is generally more active than the processes opposed to it, inasmuch as the conditions favouring nitrification are more generally present in soils.

J. Stoklasa and E. Vítek [4] attribute the reduction of nitrates to the hydrogen produced, along with carbon dioxide, in the breaking down of carbohydrates and organic acids. *Clostridium gelatinosum*, a soil organism, was found to be active in converting nitrates into ammonia and partly into proteids.

Gaspare Ampola [5] considers that denitrification in soil can be almost wholly avoided by not applying nitrates until the organic substances have been decomposed and the denitrifying bacteria thus reduced to inaction. He found that calcium nitrate offered greater resistance to denitrifying organisms than did sodium nitrate.

R. Perotti [6] gives a new method for the isolation of nitrifying micro-organisms, this being a modification of Omeliansky's plan. Blocks of commercial magnesium carbonate are used and fitted into Petri dishes or in test-tubes. The upper surface is polished smooth and the under surface is hollowed out to allow of the nutritive solution being used. After sterilisation of the block and nutrient solution, the liquid containing the micro-organisms is poured over the surface of the block and the whole kept at 28—30°. The surface of the block after a time shows small regular excavations, the magnesium carbonate being here coloured yellow, and the bacteria can then be examined microscopically.

[1] *Bied. Centr.*, 1905, **34**, 433.
[2] *Centr. Bakt. Par.*, 1905, **14**, [ii], 582.
[3] *Ibid.*, 1904, **13**, [ii], 706.
[4] *Ibid.*, 1905, **14**, [ii], 102.
[5] *Gazzetta*, 1904, **34**, [ii], 301.
[6] *Atti R. Accad. Lincei*, 1905, **14**, 1, 228.

Assimilability of Nitrogen Compounds by Plants.

Following closely on the foregoing, comes the consideration of the relative assimilability of different forms of nitrogen compounds by plants. L. Lutz[1] finds that amides are the most readily assimilable compounds, and, working with *Aspergillus niger*, *Aspergillus repens*, and *Penicillium glaucum*, he obtained higher numbers than with Raulin's solution containing ammonium salts. The next best were amines, and then nitrites. From this he deduced that the simpler the molecule the better source of nitrogen will it be for plants. On the other hand, O. Treboux[2] considers amino-acids and amides suitable for the lower green plants, but that the value of amino-acids is much less for the higher plants. He holds that nitrites are satisfactory in alkaline solutions, but poisonous in acid ones, although this effect is only noticed when a certain concentration is reached. Nitrates, he considers, have an equal or greater nutritive value than nitrites, whilst ammonium salts are better than either, and would seem to be the best form in which to apply nitrogen for chlorophyllous plants.

Green-manuring

At the Woburn Experimental Farm,[3] the subject of green-manuring has been further investigated, and mainly in reference to the question as to whether in actual practice advantage is to be derived from the growing and ploughing-in of a leguminous green crop as against a non-leguminous one. As mentioned last year, no better corn crop was obtained when following tares ploughed-in than when coming after mustard similarly treated, although it was found that the tares supplied more nitrogen to the land. To give this time to become available, a second corn crop (barley) was taken in 1904 after the wheat crop following the green-manuring. The results of the two years were :

	1903. *Wheat.* Produce per acre.		1904. *Barley.* Produce per acre.	
	Corn.	Straw.	Corn.	Straw.
	Bushels.	Cwt. qr. lb.	Bushels.	Cwt. qr. lb.
After tares ploughed-in, mineral manures used	17·8	18 1 26	18·5	11 0 4
After mustard ploughed-in, mineral manures used	37·9	37 0 8	19·7	11 2 14
After tares ploughed-in, without mineral manures	18·1	19 0 8	18·3	9 3 13
After mustard ploughed-in, without mineral manures	27·4	27 3 16	18·7	12 0 21

[1] *Compt. rend.*, 1905, **140**, 665. [2] *Chem. Centr.*, 1905, i, 619.
[3] *J. Roy. Agric. Soc.*, 1905, **66**, 198. Compare *ibid.*, 1903, **64**, 335.

From this it will be seen that even with a second corn crop the advantages of ploughing-in a leguminous crop as against a non-leguminous one have not been brought out. This investigation is being continued and, simultaneously, experiments in pot-culture with the soil of the field where the practical trial was carried out are now in progress. It is a point of the greatest importance that the results of scientific inquiry which are obtained in the laboratory should be submitted to practical test in the field under the conditions of ordinary farming, as in that way alone can they become of more than theoretical interest or confer a real benefit on agriculture.

Errors attending Pot-culture Work.

In the course of watching the progress of pot-culture experiments carried on in conjunction with field experiments on one and the same question, it has become increasingly evident that there are in pot-culture investigations a considerable number of precautions that have to be observed, the neglect of which may lead to the forming of quite erroneous conclusions, and that there are many disturbing elements any of which may vitiate an experiment, and which have to be carefully eliminated. With the extension of the pot-culture system and the mass of results now put out, it is not too much to say that these call for stricter examination than has perhaps been bestowed in the past, and it is very certain that pot-culture experiments need not only duplication but also repetition before they can be fully accepted. O. Lemmermann[1] points out that diminished growth of plants in pots is not due so much to the limited space at their disposal as to the nutritive conditions attaching to the volume of soil, and that the amount of water is frequently the most important factor. At the Woburn Experimental Station, experience has shown that in preparing different soils for pot-culture work they have to be differently treated according to their nature, and that no hard and fast lines can be laid down, but that experience alone can decide such points. With a damp or wet soil, it is impossible to fill it into pots so as to get the particles in a sufficient degree of fineness to allow of equal consolidation and aëration, and want of agreement between duplicate pots will certainly result. With a fine dry soil, in which the particles pack closely together, there is also difficulty, as the whole sets into a mass, and it is impossible to ensure a uniform distribution of moisture. Want of agreement between duplicates is sure to arise from this cause. The way in which soil is filled into pots will, again, make great differences, and is in many cases responsible for variable results. The right amount of compression to give, and how to avoid the formation of distinct

[1] *J. Landw.*, 1905, **53**, 173.

layers, each different in character and along which the water may run or collect, are matters to which great attention must be given in pot-culture, and in which only experience can be the guide. Regularity and method in water supply, the avoidance of rapid change of temperature, and many other points have to be considered, and experience at Woburn has shown that while duplication of experiment is absolutely necessary, triplication is still better, followed by repetition in a succeeding year. The differences between the results of pot-culture experiments and those of field trials can, in the great majority of cases, be traced primarily to the difficulty of reproducing in pot-culture the conditions which exist in the field, and to the non-observance of necessary precautions, or failure to check results by duplication and repetition.

Oxidation in Soils.

E. J. Russell,[1] a preliminary account of whose work was given last year, has set out the results of his examination of a number of soils from different parts, including Rothamsted and Woburn, and has shown that his method of determining their rate of oxidation as a measure of their "bacterial activity" has given results in harmony with the experience and records of the respective productive power of the soils. The rate at which oxygen is absorbed increases with rise of temperature, the amount (up to a certain point) of water, and the amount of calcium carbonate. These being the conditions that favour fertility, the rate of oxidation may be used as a measure of the fertility, and, it is suggested, of the activity of the micro-organisms.

Sterilisation of Soil.

F. Nobbe and L. Richter[2] applied ether and hydrogen peroxide to soil in which peas were growing, but this failed to exercise any sterilising influence on it, the result of application being favourable rather than otherwise. Other experiments with oats grown in pots failed to show any sterilisation when ether, benzene, carbon disulphide, and chloroform were used on the soil. C. Schulze[3] grew oats and mustard in normal soil and in soil sterilised by heating at 125°. Variable results were obtained according to the nature of the original soil. Thus, sterilisation had least injurious effect in the case of rich garden soil, and less in meadow than in arable soil, mustard being much more sensitive than oats. The injurious effect of sterilisation was found to be entirely removed by applying calcium carbonate.

[1] *J. Agric. Science*, **1**, Oct., 1905, 261.
[2] *Landw. Versuchs-Stat.*, 1904, **60**, 433.
[3] *Bied. Centr.*, 1904, **33**, 748.

Availability of Soil-constituents.

H. Ingle,[1] a short notice of whose work was given last year, has put out the results of his inquiry into the condition of a soil which had been extracted with a 1 per cent. solution of citric acid (Dyer's method), and finds that on subsequently growing plants in it there is a restoration, in available form, of potash and phosphoric acid to greater extent than that in which they originally existed. Hence Dyer's method does not give accurately the relative fertility of different soils, as it leaves out of account the relative rapidity with which the available plant food is being renewed by the natural processes of weathering and decay.

J. König[2] compares the amounts of potash and phosphoric acid soluble respectively in cold hydrochloric acid (sp. gr. 1·15) and in 1 and 2 per cent. solutions of citric acid, and finds that the results are very irregular when taking ten different soils. From this he argues that the nutritive constituents occur in very different forms. He further compares the results of pot experiments on barley with an examination of the soil used, but extracted with 2 per cent. citric acid. The citric acid was found to have dissolved much more potash and phosphoric acid than was taken up by the barley plant.

Root Secretions.

D. N. Prianischnikoff,[3] when experimenting on the assimilation of phosphoric acid, found that gramineous plants like rye and wheat could hardly avail themselves of the phosphates supplied in crude mineral phosphates, whilst lupins did nearly as well as when bone phosphate was applied. If this difference of behaviour were, he says, found to be proportional to the production of carbon dioxide by root respiration, it would support the contention that the dissolving action of roots is due to carbon dioxide alone, and does not depend on the presence of any free organic acids.

J. Stoklasa and A. Ernest[4] have estimated the amount of carbon dioxide in soils which is produced in the respiration of bacteria, moulds, algæ, and by the roots of plants, the quantity from the last-named source being about sixty kilograms per hectare per diem. The authors consider the action of roots, especially the young roots, on the mineral substance of the soil to be due to the carbon dioxide evolved and not to organic acids. P. Kossowitsch[5] (who has shown that

[1] *Trans.*, 1905, **87**, 43.
[2] *Landw. Versuchs-Stat.*, 1905, **61**, 371.
[3] *Bied. Centr.*, 1905, **34**, 741.
[4] *Centr. Bakt. Par.*, 1905, **14**, [ii], 723.
[5] *Bied. Centr.*, 1905, **34**, 367.

organic acids are not secreted by roots) also finds that the amount of carbon dioxide given off by the roots of mustard is very considerable in relation to the ash constituents of the plant. He is uncertain as to whether the carbon dioxide only acts on the soil or whether it has other functions as well.

Plant Food removable from Soils by Water.

In America, the examination of soils by the methods described in last year's report has been continued, and the Bureau of Soils of the U.S. Department of Agriculture has issued the results of further investigations by F. H. King,[1] chief of the division of Soil Management, in addition to which this investigator has issued other papers of his own.[2] He deals mainly with the amounts of plant food which are readily recovered from field soils by taking the first four feet of the soil and washing it for three minutes with distilled water; he then compares the amounts of potash, lime, magnesia, phosphorus, and nitrogen removed with the amounts of these constituents which crops would remove. Applying this method, he shows that the three-minute treatment would remove enough nitrogen to provide that needed by a two-and-a-half ton per acre crop of clover hay, enough potash for two, and enough phosphoric acid for five such crops. King next considers the relation of crop-yields to the amounts of plant-food materials which are removed from the soils by successive washings with distilled water, and concludes that there is a remarkable concordance between the crop-yields and the potash recovered as soluble salts, whilst, if the total salts recovered in the washing be taken, it will be found that larger amounts are recovered according as the crops have given the higher yields.

Nitrates removed from Arable Soils.

R. Warington[3] has made a useful and full survey of the production and loss of nitrates in the soil, this being drawn from a study of typical plots of the Rothamsted experiments. After accounting for the nitrogen removed in the subsoil drainage water and in the crop, he shows that there remains a considerable surplus of nitrates which have been formed in the surface or added as manure, but which is not accounted for. He investigates the probable causes of this disappearance, and, after allowing that a certain small proportion may disappear through denitrification, shows that there must be other reasons for the loss. In spring, there was stored up in the surface soil a large amount of nitrates for the use of the wheat crop, and yet the drainage water

[1] *U.S. Dept. Agric. Bureau of Soils, Bull.* No. 26, 1905.
[2] "Investigations in Soil Management," F. H. King, Madison, Wis., 1904.
[3] *Trans. Highland Agric. Soc. of Scotland*, 1905, 148.

showed a diminished amount of nitrates, this disappearing almost entirely in the first week of May. Moreover, the crop, although having this store at hand, did not at harvest contain more than one-half the amount. And in reply to the question as to what becomes of this nitrogen, Warington hints at an actual loss of nitrogen taking place in the growing plant itself.

Action of Nitrates and Ammonium Salts on Soil.

The relative action of sodium nitrate and ammonium salts in regard to the condition in which they leave the soil to which they are severally applied has received considerable attention of late. P. Kossowitsch[1] states that when nitrates are used the plant takes up more acid than base, and that an alkaline substratum is produced which, if not neutralised, might cause injury to the development of the plant. When ammonium salts, on the other hand, are used, an acid substratum is produced, and this needs neutralising by the presence of calcium carbonate, for example. This is borne out by the results obtained at the Woburn Experimental Farm,[2] where the continued use of ammonium salts on a soil originally containing very little lime has brought about an acid condition of the soil and complete sterility. On the application of lime, the acidity was neutralised and fertility at once restored. In 1904, the difference between the barley crop of limed and unlimed plots where ammonium salts had in each case been used continuously was as much as twenty-four bushels per acre. Similarly, it may be noted that on this same soil sodium nitrate continuously applied, although not producing sterility as quickly as ammonium salts, is clearly beginning to show exhaustion of the soil and diminished produce both with wheat and barley.

A. D. Hall[3] deals with this same question and shows, from the experience of soils at Rothamsted, the importance of calcium carbonate in acting as a base towards the acids produced by bacterial activity. He has measured the rate of removal of lime from unmanured arable land, and shows that this amounts to 800—1000 lbs. per acre yearly in a soil containing 1 per cent. of calcium carbonate. This loss is further increased by the use of ammonium salts, but is diminished by using nitrates or dung, the former conclusion accordingly bearing out the results already obtained at Woburn. The restoration to the soil, by the growing plant itself, of the bases of the neutral salts on which it feeds, or the formation of bases by the action of certain bacteria in the soil on organic salts, Hall points out can alone explain that soils containing only a very little calcium carbonate can retain their neutral

[1] *Bied. Centr.*, 1905, **34**, 378. [2] *J. Roy. Agric. Soc.*, 1905, **66**, 197.
[3] *Brit. Assoc. Report*, S. Africa, 1905, Section B.

reaction and maintain their fertility. When, however, excess is reached, as in the case of the Woburn soils, sterility will ensue.

Organic Matter in Soils.

A. Mayer[1] finds that the humic acids of brown sandstone contain less carbon than those of grey sand. He considers that these acids are oxidised to insoluble ferric salts when ferric oxide is present. E. Blanck,[2] in giving complete analyses of a number of black soils from East Prussia, states that these contain much less humus than do the black soils of Russia. A new and rapid method of determining the organic matter in soils has been introduced by J. H. Pettit and T. O. Schaub,[3] this consisting of a modification of Parr's method of combustion with sodium peroxide, and subsequent determination of the carbonate formed. Magnesium is used to start the reaction, and the results obtained are practically identical with those given by combustion with copper oxide.

Colloids in Soils.

B. Sjollema[4] estimates approximately the amount of colloids in soils by treating them with a solution of methyl-violet (0·1—0·2 gram in 500 c.c.). The colloids are dyed, but not the quartz. The use of different dyes enables further distinction to be made between various colloids. Sjollema also describes a means of isolating the colloid substances of soils.

Lime and Magnesia in Soils.

Mention has been made of work bearing on the importance of having a sufficiency of calcium carbonate present in soils, as also of A. D. Hall's estimate of the rate of removal of lime from soils. Th. Dietrich,[5] working on Hessian soils, found the application of lime (either as burnt lime, marl, or dolomite) to be beneficial on sandy land and sandy loams. Calcium silicate could not, however, be used in place of calcium carbonate.

O. Loew and K. Asō,[6] continuing their work on the ratio of lime to magnesia in soils in order to produce the best results, state that the ratios previously given (1 for most cereals and 1 : 3 or 4 for leafy crops) only hold good when the lime and magnesia are present in the soil in

[1] *Landw. Versuchs-Stat.*, 1904, **60**, 475.
[2] *Ibid.*, p. 407.
[3] *J. Amer. Chem. Soc.*, 1904, **26**, 1640.
[4] *J. Landw.*, 1905, **53**, 67 and 70.
[5] *Bied. Centr.*, 1904, **33**, 814.
[6] *Bull. Coll. Agr. Tōkyō*, 1905, **6**, 336.

equally available forms, as, for example, carbonates. If calcium were present as carbonate and magnesium as sulphate, the ratio would be very different, and more like 7 : 1.

Loew,[1] in another paper, says that an excess of lime is in most cases rendered harmless by being converted into oxalate, but that an excess of magnesium will retard growth.

On the other hand, Fr. Gössel,[2] in experiments carried out on water and soil-culture, obtains no confirmation of Loew's theory as to there being any need of a fixed relation between lime and magnesia, but thinks that the influence of lime is determined principally by the character of the soil.

Phosphates.

F. Mach[3] made experiments on the solubility of iron, aluminium, and calcium phosphates in water, water containing hydrated silica, water with humic acid, and in a saturated solution of carbon dioxide. All were dissolved to a slight extent with water, and water containing hydrated silica dissolved aluminium phosphate still more. But water with humic acid was two to three times as powerful, whilst a saturated solution of carbon dioxide dissolved twice as much calcium phosphate as did plain water, although it was not effectual on either ferric or aluminium phosphates.

G. Gray[4] has investigated the retrogression of soluble phosphates in mixed manures in which bone dust, basic slag, lime, and other materials have severally been used with superphosphate. In a mixture of superphosphate and bone dust retrogression is small and proceeds but slowly, none taking place until about twelve days have passed. The citrate-soluble phosphate is increased at the expense of the insoluble phosphate. With basic slag, more than 50 per cent. of the soluble phosphoric acid reverts within three hours to the insoluble form, 77 per cent. in twenty-four hours, and 85 per cent. in six days. With slaked lime, 94 per cent. becomes insoluble within three hours, and the whole within twenty-four hours, the dicalcic phosphate being formed. When superphosphate and kainite are mixed, there is but slight retrogression, this not exceeding 7 per cent. in eighteen days and being due mainly to the salts of magnesium present in the kainite.

Potash and Soda.

Schneidewind and Ringleben's[5] conclusions in favour of the use, on a soil poor in lime, of pure potassium salts in preference to kainite as a

[1] *Bied. Centr.*, 1905, [ii], 412. [2] *Ibid.*, 1904, [ii], 1157.
[3] *Chem. Centr.*, 1904, ii, 1164.
[4] *Trans. Australasian Assoc. Adv. Science*, 1905, 157.
[5] *Landw. Jahrb.*, 1904, **33**, 353.

manure for potatoes have been confirmed at the Woburn Experimental Station,[1] where better crops of potatoes were obtained by using 1 cwt. of potassium sulphate per acre than with 4 cwt. per acre of kainite, and this whether sodium nitrate or ammonium sulphate was used (along with superphosphate). The soil is a sandy loam deficient in lime. H. C. Prinsen-Geerligs,[2] in working on the influence of potassium and sodium salts as manures for sugar cane, found that potassium could not be replaced by sodium, for on a soil as free as possible from potassium the plants would not grow, although watered regularly with sodium chloride solution. The sugar cane was found to take up very little sodium in its normal growth, the chlorine in it being combined mainly with potassium. If the soil was treated with sodium chloride, potash was liberated and rendered available as plant food.

P. Wagner[3] and others showed that potassium salts containing much chlorine caused considerable increase in barley and beet, and especially in the leaves of mangels and potatoes. H. Süchting[4] states that the harmful influence of sodium chloride on potatoes is due to the chlorine and not to the sodium, inasmuch as sodium carbonate in moderation did not injure the crop. Sodium is equally distributed through the plant during the vegetative period, but towards the end of this it accumulates in the leaves.

Farmyard Manure.

E. J. Russell,[5] in conducting a feeding experiment in which linseed-cake with other foods was given to bullocks, analysed the dung when removed from the feeding boxes in which it had been made. The loss of nitrogen in making the dung was 14·6 per cent., this value being in fair agreement with Voelcker and Hall's[6] results (15·87 per cent.) recently obtained. In trying to ascertain how the loss of nitrogen of urine could be avoided, E. Böhme,[7] by the use of gypsum (10 per cent.), reduced this loss to 7 per cent. in 250 days, whilst the urine by itself lost 56 per cent. of its nitrogen in that time. One per cent. of sulphuric acid gave a loss of 5·5 per cent. only, and by using 2 per cent. of sulphuric acid the whole of the nitrogen was retained.

Influence of "Rarer" Constituents of the Soil.

The work on this subject has been continued at the Woburn Experimental Station, by Loew and others at Tōkyō, and by other investigators on the Continent. At Woburn,[8] the influence of

[1] *J. Roy. Agric. Soc.*, 1905, **66**, 203.
[2] *Chem. Centr.*, 1905, i, 897.
[3] *Bied. Centr.*, 1905, **34**, 435.
[4] *Landw. Versuchs-Stat.*, 1905, **61**, 397.
[5] *Report S.E. Agric. Coll., Wye*, 1905.
[6] *J. Roy. Agric. Soc.*, 1902, **63**, 88.
[7] *Bied. Centr.*, 1905, **34**, 300.
[8] *J. Roy. Agric. Soc.*, 1905, **66**, 206.

manganese and iron sulphates on wheat and barley has been studied, both by soaking the seed, before sowing, in solutions of the salts, and by direct application of the salts in solution to the growing crop. In the case of wheat, the soaking of the seed improved the germination so long as the strength of solution did not exceed 2 per cent., but increase of yield was only obtained from soaking in a 2 per cent. or 5 per cent. solution of ferrous sulphate. By direct application to the growing plant, manganese sulphate up to ½ cwt. per acre and ferrous sulphate up to 1 cwt. per acre increased the yield. In the case of barley, soaking of the seed did not injure germination, but produced no benefit, whilst solutions of both manganese and ferrous sulphates, more particularly the latter, produced some increase of crop.

These experiments with manganese have been confirmed lately by others carried out on oats by G. Bertrand[1] on a soil which contained 0·057 per cent. of manganese. Two plots were selected and received the usual fertilisers, but to one of them manganese sulphate at the rate of fifty kilograms per hectare was added. This plot gave an increase of 22·5 per cent. in the total crop over the plot receiving no manganese. Bertrand made analyses of the oat grain, and these showed that the grain from the manganese plot contained less moisture and slightly less nitrogen than that from the other plot, and it also had a higher bushel-weight.

E. Haselhoff[2] investigated the action of sulphur dioxide, zinc oxide, and zinc sulphate on soils and plants. Sulphur dioxide was rapidly converted into sulphuric acid and did not injure soils. Zinc oxide (0·2 per cent.) had a slightly stimulating effect on wheat, but zinc sulphate was extremely injurious. The same observer found that 0·1 gram of ammonium thiocyanate (in 8·5 kilograms of soil) acted injuriously with oats, wheat, and mustard, whilst 0·2 gram almost entirely prevented any yield, the quantity proving injurious even when applied twelve weeks before the seed was sown. L. L. Harter[3] showed that magnesium sulphate, magnesium chloride, and sodium sulphate all act as stimulants to wheat when used in dilute solutions, but that sodium carbonate and sodium chloride will not. Also that traces of zinc will kill the root tips in twenty-four hours. Lastly, Y. Yamano[4] ascertained by pot-experiments on barley and flax that moderate amounts of aluminium salts have a stimulating effect on plant development. In water-cultures, 0·2 per cent. of alum, however, acted injuriously after three weeks, whilst 0·8 per cent. killed the plants in a few days.

[1] *Compt. rend.*, 1905, **141**, 1255.
[2] *Bied. Centr.*, 1905, **34**, 24 and 31.
[3] *U.S. Dept. Agric.*, 1905, *Bur. Plant Ind.*, *Bull.* No. 79.
[4] *Bull. Coll. Agr. Tōkyō*, 1905, **6**, 429.

Germination.

The question has been asked whether it is possible for germination to take place in absence of air. According to experiments by T. Takahashi,[1] rice—accustomed to grow in swampy ground—will grow in water alone, in absence of air and without sugar being added. W. Windisch and K. Schönewald[2] controvert Nilson's theory that germination of barley depends on the activity of bacteria on the surface of the corns. They show that barley can be completely sterilised by treatment with mercuric chloride solution in alcohol and yet not lose its vitality, the subsequent germination being quite satisfactory.

P. Becquerel[3] has investigated the action of liquid air on seeds, coming to the conclusion that their power of resistance to low temperatures depends on the amounts of water and of gas present in the tissues. If the protoplasm has, through drying, reached its maximum of concentration, it can resist the action of low temperatures, and does not freeze, but retains its germinating power; when, however, a certain amount of water and gas are present, the protoplasm and nucleus become disorganised by the cold.

Assimilation.

Cr. Bernard,[4] while not denying that the decomposition of carbon dioxide by plants may come from the action of ferments, shows that when chlorophyll and extracts of plant tissues are mixed, no evolution of oxygen takes place in sunlight. If bacterial decomposition sets in, gaseous products are obtained, but not oxygen. F. F. Blackman and G. Matthaei[5] have given the factors which control assimilation of carbon dioxide by leaves as being (1) intensity of illumination, (2) temperature of leaf, (3) pressure of gas in surrounding air. The endeavour is made to interpret the variations which occur in the amount of assimilation in terms of these three factors. Leaves of different plants are found to vary with increased temperature, and there does not seem to be any optimum intensity of light for assimilation. A. Kanitz,[6] working on the same subject, shows that up to 37° the rate of assimilation increases regularly with the temperature, but after 37° the ratio diminishes rapidly.

The principal contributions to the subject of the assimilation of carbon dioxide by green leaves consist, however, in the series of papers by

[1] *Bull. Coll. Agr. Tōkyō*, 1905, **6**, 439.
[2] *Woch. Brau.*, 1905, **22**, 200.
[3] *Compt. rend.*, 1905, **140**, 1652
[4] *Ibid.*, 509.
[5] *Proc. Roy. Soc.*, 1905, **76**, Series *B*, p. 402.
[6] *Zeit. Elektrochem.*, 1905, **11**, 689.

Horace T. Brown and F. Escombe,[1] presented to the Royal Society. These have special reference to the rate of assimilation and to the interchange of energy between the leaf and its environment. A new method of determining the rate of assimilation is described, and the results are compared with those obtained by Sachs' weighing method. The rate of assimilation is measured by passing a known volume of air over a leaf surrounded by an atmosphere containing a normal but ascertained amount of carbon dioxide, and by subsequently ascertaining, by analysis, what increase of carbon dioxide there has been. The authors criticise Sachs' method and point out sources of error in it which led him to place the rate of assimilation much too high. The results they now obtain by the direct method of estimation are considerably lower than Sachs' figures. One source of error would seem to lie in the adding—as Sachs did—of the hourly gain of weight during the day to the hourly loss during the night in order to arrive at the result. Brown and Escombe also point out that experiments such as these cannot be carried out in full sunshine, but must be made either on dull days or by moderating the sunshine by a thin canvas screen. They further discuss the differences between experiments made on detached leaves and those on attached leaves freely exposed to the air, and show that the rate of assimilation is much greater with the detached leaves. In considering the "energetics" of the leaf, many factors have had to be determined, for example, the total incident radiation, its absorption by the leaf, the thermal emissivity of the leaf-lamina, &c., and details are given as to how these have been severally estimated. It is shown, from experiments with a sunflower leaf, that of the total incident energy only 0·66 per cent. is used in the work of actual assimilation or production of new material.

J. Friedel,[2] working on chlorophyllous assimilation, found that this can take place when the atmosphere contains no oxygen. On exposing a leaf of *Euonymus japonicus* to light in a tube containing only carbon dioxide and nitrogen, carbon dioxide was absorbed and oxygen evolved.

G. Plancher and C. Ravenna[3] discuss the evidence in favour of the formation, in the early stages, of formaldehyde in the manufacture of starch by chlorophyllous plants, but on distilling extracts of leaves they obtained no indication of the presence of either free or combined formaldehyde in the green tissues. P. Mazé and A. Perrier[4] found that sugars, glycerol, and methyl and ethyl alcohols retarded the germination of maize seeds, but did not prevent the growth of the young plants. Sugars were assimilated in the light, also glycerol, but the latter hindered development. Whilst methyl alcohol helped the activity, ethyl alcohol was harmful, probably owing to production of aldehyde.

[1] *Proc. Roy. Soc.*, 1905, **76**, Series *B*, 29. [2] *Compt. rend.*, 1905, **140**, 169.
[3] *Atti R. Accad. Lincei*, 1904, **13**, [ii], 459. [4] *Ann. Inst. Pasteur*, 1904, **18**, 721.

Different plants varied generally in regard to their behaviour to alcohols.

The effect of growing plants in an atmosphere rich in carbon dioxide was ascertained by E. Demoussy [1] to be an increase in the amount of dry matter in the plant.

Plant Constituents.

E. Charabot and G. Laloue [2] find that in an annual plant the essential oil migrates from the leaves to the flowers along with the carbohydrates. After fructification, the essential oil returns to the leaves.

E. Schulze [3] has determined the amount of non-proteid nitrogenous substances in plants. In seeds, this varies very greatly, being highest in leguminous and lowest in cereal and oily seeds. Etiolated plants will contain either asparagine or glutamine, asparagine being found in the case of leguminous seedlings and in cereals and grasses, whilst glutamine occurs in etiolated plants of sunflower, white mustard, rape, cress, radish, &c.; glutamine, however, does not exceed 2·5 per cent. in the dry matter, but the proportion of asparagine may be as high as 25 per cent. In roots and tubers, the conditions are much the same as in etiolated plants, and asparagine and glutamine are the most abundant amides. Many other amides are noted as occurring in different roots and tubers.

The proteids of wheat have been investigated by T. B. Osborne and I. F. Harris,[4] and Kutscher's view that the proteid soluble in alcohol consists really of two proteids is rejected. The authors consider it to be a single substance and give to it the name "gliadin"; it contains an amount of glutamic acid much in excess of that obtainable from any other proteid, and possibly on this account special importance attaches to it when considering wheat as a food. The same authors have examined the methods of fractional precipitation of proteins by ammonium sulphate, and come to the conclusion that whilst it affords in many cases a useful means of separation, it cannot be used for distinguishing vegetable globulins from vegetable albumins.

T. B. Osborne, with L. B. Mendel and I. F. Harris,[5] have investigated the nature of the proteins of castor bean, and especially in regard to the toxic substance *ricin*, believed by Stillmark (who isolated it) to be a globulin, but the protein nature of which has been questioned by other investigators, notably Jacoby. The authors show that the castor bean seed contains (1) a considerable quantity of a crystallisable

[1] *Compt. rend.*, 1904, **139**, 883.
[2] *Ibid.*, 928.
[3] *J. Landw.*, 1904, **52**, 305.
[4] *Amer. J. Physiol.*, 1905, **13**, 35.
[5] *Ibid.*, **14**, 259.

globulin, (2) a much smaller amount of a coagulable albumin, and (3) proteoses. The toxic properties ascribed to ricin are to be associated with the coagulable albumin of the castor bean, and the investigation affords no reason for denying the identity of ricin with the coagulable albumin of the seed.

The increase of proteid formation during the ripening of seeds has been investigated by W. Zaleski[1] and by G. André.[2] Vegetable albumin was not found in white lupin seeds when they first began to form, but when they were mature the nitrogen in this form was 2·5 per cent. of the total. Legumin similarly, although absent at first, in the ripe seed gave nitrogen up to 10 per cent. of the total.

C. von Seelhorst and Fresenius,[3] by carrying out pot-culture experiments on oats in which variable amounts of water were supplied, ascertained that as the moisture increases the proteid nitrogen diminishes less than the total nitrogen, but that the digestible proteid nitrogen diminishes more than the total proteid nitrogen. Hence, in a dry season one would expect the feeding value of oat straw to be higher than in a wet season.

L. du Sablon[4] explained why assimilation in the case of evergreens is relatively feeble but continues all the year, by showing that the maximum of reserve substances is attained at the beginning of spring, whilst the minimum is reached about July or August. With caducous trees, on the contrary, the maximum is in the autumn.

B. Schulze[5] shows the difference between rye and wheat in regard to the time at which they assimilate nitrogen and phosphoric acid. Rye by the end of winter will have taken up nearly one-half of its full supply of nitrogen, whilst with wheat assimilation of nitrogen takes place mostly from the beginning of April to the time of seed formation. Phosphoric acid is taken up by rye mostly in spring, and with wheat from spring to flowering time. A certain amount of potash is taken up by both plants during winter, but the greatest assimilation is at the time of greatest production of carbohydrates.

The last paper written by H. Wilfarth[6] (he died on Nov. 27, 1904), the former colleague of Hellriegel, was in conjunction with H. Römer and G. Wimmer, and had reference to the assimilation by plants of their nutritive substances at different stages of their growth. Barley, spring wheat, peas, and mustard were found to assimilate most of their nutritive substances by the time of flowering, but with potatoes this went on until the crop was ripe. Further, the mineral constituents in the case of the barley, wheat, peas, and mustard were, with the exception of phosphoric acid, returned to more or less extent to the soil, but

[1] *Chem. Centr.*, 1905, i, 1606.
[2] *Compt. rend.*, 1905, **140**, 1417.
[3] *J. Landw.*, 1905, **53**, 127.
[4] *Compt. rend.*, 1905, **140**, 1608.
[5] *Bied. Centr.*, 1905, **34**, 602.
[6] *Landw. Versuchs-Stat.*, 1905, **63**, 1.

this was not the case with potatoes. Starch increased up to the ripening period in all the plants except mustard, its place in the latter being taken by fat.

Enzymes.

J. Stoklasa [1] has isolated from the sap of the beet-root, potato, and pea an enzyme which produces alcoholic fermentation and the formation of lactic acid in dextrose solutions. This enzyme he terms "lactolase," and considers it now definitely settled that the process of anaërobic respiration in the plant cell is an alcoholic fermentation accompanied by the formation of lactic acid, the anaërobic metabolism being identical with fermentation by yeast. Aërobic respiration he holds to be a secondary phenomenon.

In the case of the ripening seeds of peas, W. Zaleski [2] has investigated the nature of the proteolytic enzymes present, and states that it is uncertain whether the ripening seeds contain only one ferment of a tryptic nature or whether they contain several, including trypsin itself.

Glucosides.

Considerable attention has been directed to the poisonous properties which certain seeds, generally of imported origin, and used occasionally as food for cattle, are known to possess at times. Among these are the coloured seeds of the wild *Phaseolus lunatus*, which are variously known in commerce as "Rangoon beans," "Java beans," &c. W. R. Dunstan [3] has investigated these and finds the seeds to contain a cyanogenetic glucoside, which undergoes hydrolysis, forming hydrocyanic acid as one of its products. This glucoside Dunstan has isolated, its formula being $C_{10}H_{17}O_6N$, and he gives to it the name "Phaseolunatin." He further separated the hydrolytic enzyme of *Phaseolus lunatus*, which he thinks is probably emulsin. It is worthy of notice that the glucoside is not found in the plant after cultivation, the seeds of the cultivated plant being white, and not poisonous at all.

Other workers have similarly found cyanogenetic glucosides in the examination of other plants. Thus, F. Power and F. Lees [4] found in the seeds of *Gynocardia odorata* a new glucoside which they call "gynocardin," and they further separated the enzyme "gynocardase." L. Guignard,[5] as also E. Bourquelot and E. Danjon,[5] separated from the leaves of *Sambucus nigra* a glucoside which, when acted on by emulsin, yielded dextrose, hydrogen cyanide, and an aldehyde. Guignard believed the glucoside to be amygdalin. Subsequently, Guignard [6] ascertained

[1] *Chem. Centr.*, 1905, i, 265.
[2] *Ibid.*, 1606.
[3] *Proc. Roy. Soc.*, 1905, **72**, Series *B*, 285.
[4] *Trans.*, 1905, **87**, 349.
[5] *Compt. rend.*, 1905, **141**, 16, 59, and 236.
[6] *Ibid.*, 448.

that the leaves of the red currant yielded a little hydrogen cyanide at all periods of vegetation, although other species of *Ribes* did not. In the leaves of *Thalictrum aquilegifolium*, L. van Itallie [1] found a glucoside resembling phaseolunatin; this was not found, however, in other species of *Thalictrum*.

Influence of Variety.

A. D. Hall,[2] when dealing with the question of "strength" in wheat, and the various efforts which are being made to introduce into this country a wheat of equal yielding value to English varieties, but the grain of which possesses the "strength" of Canadian and other varieties, draws attention to the importance attaching to "variety." While climate, soil, season, and manuring may all exercise a certain modifying influence, this is at best small when compared with the intrinsic characteristics impressed on the plant, and which constitute what we term "variety."

T. B. Wood and R. A. Berry [3] have, for instance, shown the variations which occur in the chemical composition of mangels, and S. H. Collins [4] has done the same in respect of swedes; but in each case the predominating factor was that attaching to variety. Hence improvement, alike in cereals and in root-crops, has to be looked for in the breeding of new varieties by careful selection. Hall, in the paper just referred to, shows the difficulties of determining in what the "baking value" of wheat lies and how it is to be estimated, for, whilst the use of nitrogenous manures sends up the percentage of nitrogen and dry gluten as a rule, the baking value is generally deteriorated. The determination of total nitrogen or of gluten obtained by washing out the starch does not give the baking value, nor is this obtained by ascertaining the percentage of gliadin (nitrogen soluble in alcohol), or the relation of gliadin to glutenin. In Canada, both Synder and F. T. Shutt [5] have worked at the same question, but without being able to differentiate accurately, by chemical means, between different grades of wheat.

Water.

For the purification of water supplies, G. T. Moore [6] has adopted a method of treating water with copper sulphate in the proportion of 1 to 5,000,000. The growth of algæ is prevented by this, sewage bacteria are destroyed, and the total number of bacteria very greatly reduced. Experiments by H. Kraemer confirm the efficiency of the treatment,

[1] *J. Pharm. Chim.*, 1905, [vi], **22**, 337.
[2] *Brit. Assoc. Reports*, S. Africa, 1905, Section B.
[3] *J. Agric. Sci.*, **1**, May, 1905, 176.
[4] *Ibid.*, Jan., 1905, 89.
[5] *Centr. Exp. Farm, Ottawa, Bulletin* No. 50, 1905.
[6] *Amer. J. Pharm.*, 1904, **76**, 553 and 574.

and it is stated that the small amount of copper in solution in the water is too little to do any harm to consumers. Kraemer in experiments with copper foil placed in water found that *Bacillus coli* and *B. typhosus* were completely destroyed.

E. Bonjean[1] carried out experiments on sterilising water with hydrogen peroxide, and was able to sterilise a litre of Seine water with 0·291 gram of hydrogen peroxide in six hours. If, however, nascent hydrogen peroxide was used, only 0·06 gram was required, and did the work in four hours.

Magnesium, when added to water containing micro-organisms, was found by F. Dienert[2] to kill the bacteria after two to three days, although pure magnesia under similar conditions was unable to destroy them.

W. G. Savage,[3] in seeking for bacterial evidence of the contamination of tidal rivers, found that the examination of the mud was more reliable than that of either the water or samples of oysters, inasmuch as the two latter only show recent contamination, whereas *Bacillus typhosus* or *B. coli* retain their characters for a long time in tidal mud. Typhoid bacilli also survive for at least two weeks in tidal mud.

Milk.

F. J. Lloyd[4] has brought to a conclusion his investigation into the causes of "flavour" in dairy products, the primary object being to ascertain what it was that produced the so-called "nutty" flavour in cheese and butter. Although the work failed to solve the mystery, many points of interest were brought out in the course of the research. It was shown, for example, that the lactic bacillus was able to continue its existence after its activity as an aërobic microbe had ceased. Further, the evidence pointed to the conclusion that an enzyme developed from the bacillus was the chief factor in the conversion of milk-sugar into lactic acid. E. von Freudenreich and J. Thoni,[5] while holding that the lactic acid bacteria have most to do with cheese-ripening, were unable to decide which of them were the most favourable. If artificial rennet alone was used, the ripening was not satisfactory, but by using suitable bacteria along with artificial rennet the ripening proceeded normally.

J. Arthaud-Berthet[6] isolated several varieties of *Oidium lactis* and studied their action. In cream, it is one of the most likely causes of rancidity of butter, and in cheese frequently causes a peculiar sickness known as "graisse." L. van Slyke and E. B. Hart[7] show that the

[1] *Compt. rend.*, 1905, **140**, 50.
[2] *Ibid.*, 273.
[3] *J. Hygiene*, 1905, **5**, 146.
[4] *Report to Board of Agriculture*, 1905.
[5] *Centr. Bakt. Par.*, 1905, **14**, [ii], 34.
[6] *Compt. rend.*, 1905, **140**, 1475.
[7] *J. Amer. Chem. Soc.*, 1905, **27**, 679.

principal cause of what is known as "mottled" butter is excess of lactic acid, as when this exceeds 5 per cent. casein lactate only is present, and not calcium casein or free casein. J. Golding,[1] who investigated the nature of a peculiar "taint" which was imparted to milk after passing through a tinned-copper cooler from which the tin was much worn off, found that copper is readily acted on by fresh milk, small quantities of the metal going into solution. Milk thus contaminated acquires a peculiar flavour which appears to be due to the development of micro-organisms in the presence of copper. T. E. Thorpe[2] has investigated the changes which take place in samples of milk kept for varying periods of time in closed bottles, and shows that by using his process for the analysis of sour milks the original composition of the milk can—in all but very exceptional cases—be ascertained with sufficient accuracy.

J. Augustus Voelcker.

[1] *J. Soc. Chem. Ind.*, 1905, **24**, 1285. [2] *Trans.*, 1905, **87**, 206.

MINERALOGICAL CHEMISTRY.

In preparing this report the writer has followed on the whole the method of treatment adopted in that of last year, for as the material under discussion consists in the main of a number of entirely disconnected facts, the construction of a continuous narrative appeared neither easy nor indeed advisable, and has accordingly not been attempted. The object in view has been rather to present in some detail points of general interest, and to touch lightly, or not at all, on matters of little moment, or likely to appeal to none save specialists; it is hoped, however, that nothing of great importance has been overlooked or omitted.

General and Physical Chemistry of Minerals.

Salt Deposits.—During the year, J. H. van't Hoff[1] and his pupils have added seven more to the long series of papers on the "Formation of Oceanic Salt Deposits." In number XXXIX, the transformation of Glauber's salt, $Na_2SO_4,10H_2O$, into thenardite, Na_2SO_4, which takes place normally at 32·4°, is shown to occur at lower temperatures if other salts are present. The limits of the existence of tachhydrite, $CaCl_2,2MgCl_2,12H_2O$, are set forth in number XL. The temperature of formation of potassium pentacalcium sulphate, $K_2Ca_5(SO_4)_6,H_2O$, is the subject of number XLI, that of glauberite, $Na_2SO_4,CaSO_4$, of number XLII. The investigation, so far as calcium compounds at 25° are concerned, is brought to a conclusion in number XLIII, and the composition of all constant solutions when saturated with the particular calcium salt with which the solutions are in equilibrium is tabulated.

The investigation of boron compounds and of the part played by calcium salts at higher temperatures is now being begun. Number XLIV deals with the limit of existence of tachhydrite at 83°, and number XLV with the occurrence of tinkal, $Na_2B_4O_7,10H_2O$, and of octahedral borax.

The study of this important work has been greatly facilitated by

[1] *Sitzungsber. K. Akad. Wiss. Berlin*, 1904, 1418; 1905, 232, 305, 478, 712, 913, 1086.

the publication by van't Hoff[1] of the first part of a connected account in book form of his researches, in which salt deposits consisting of the chlorides and sulphates of sodium, potassium, and magnesium are fully dealt with. This account has been supplemented by a long paper recently published in the *Zeitschrift für anorganische Chemie*, in which calcium compounds are considered.[2] It is therefore now possible to obtain readily a complete conception of the progress so far made towards the solution of the complex problems of salt deposits.

Constitution of the Felspars.—One of the most important contributions which has yet been made to our knowledge of the mutual relations of molten silicates is contained in a paper by A. L. Day and E. T. Allen[3] on the "Isomorphism and Thermal Properties of the Felspars." Employing refined modern methods of high temperature thermometry, the authors have traced the cooling and heating curves of albite and anorthite, and of mixtures of these substances corresponding to certain of the plagioclases. Microcline and borax have also been included in the field of observation. The melting points were determined by the changes in the cooling or heating curves caused by evolution or absorption of heat. In the case of the plagioclases, the various members studied were prepared artificially. After a preliminary examination of albite, microcline, and borax, which brought to light the important part played by viscosity in retarding crystallisation and in obscuring the phenomena, it was found that artificial anorthite melted sharply at 1532° and crystallised readily. Pure albite, on the other hand, could not be persuaded to crystallise at all, and had no definite melting point. The intermediate members of the plagioclase series gave intermediate results. Thus, the mixture Ab_1An_5 crystallised tolerably readily, and had a fairly sharp melting point at 1500°, while Ab_4An_1 was almost as intractable as pure albite. The specific gravities of these crystalline artificial felspars were also determined. The most important conclusions arrived at are as follows: (1) if the melting points of the plagioclases are plotted as ordinates and the compositions as abscissæ, a nearly linear relation is obtained. These felspars are solid solutions and form an isomorphous series belonging to type I of Bakhuis Roozeboom's classification. (2) The isomorphism is confirmed by a study of the specific gravities. (3) In the case of albite and microcline there is no definite melting point, the amorphous melted mass remaining of the same order of

[1] *Zur Bildung der ozeanischen Salzablagerungen.* Braunschweig: Vieweg u. Sohn. 1905. Pp. 85. Price 4 marks.

[2] *Zeit. anorg. Chem.*, 1905, **47**, 244—280.

[3] *Amer. J. Sci.*, 1905, [iv], **19**, 93. See also Pub. 31 of the Carnegie Institute, Washington.

viscosity as the rigidity of the crystals through a considerable range of temperature. The absorbed heat of fusion was distributed over this interval. (4) Viscous, poorly-conducting melts do not give constant solidifying points.

Mutual Relations of Fused Silicates.—The important work of J. H. L. Vogt was referred to in the report for 1904, and towards the close of that year the second half of his book entitled "Die Silikatschmelzlosüngen" appeared. In it are given the data on which were based many of the conclusions he had already announced, as well as a full discussion of many points, either new or but lightly touched on in the first portion. The subjects dealt with include: the melting points of minerals; the cooling curves of the silicates, their total and latent heats of fusion, specific heats, and radiation exponents; energy isobars; points of transformation below the melting points; experimental proof of the depression of the melting point in silicate melts containing several components; types of mixed crystals in the metasilicate series; the composition of certain eutectic mixtures; determination of molecular weights; supersaturation and resorption; relations between viscosity, time of crystallisation, and size of crystals; glass as a solid solution; felspar and quartz; theory of silicate melts and technical applications. The general position adopted may be summed up in the statement that van't Hoff's law of molecular melting point depression, Ostwald's law relative to the formation of labile compounds, Nernst's laws of the diminution of solubility by a common ion and of the heterogeneous equilibrium of two liquid phases possessing limited solubility, Bakhuis Roozeboom's laws concerning the solidifying points of mixed crystals of two substances, and the law of electrolytic dissociation, due to Arrhenius, all hold for these silicate melts.

Further, he believes that silicate melts at the ordinary pressure are crystalloidal mutual solutions of tolerably simple compounds which crystallise out on cooling. As a rule, the compounds do not polymerise. All molten silicates are mutually soluble to any extent, but between silicates and sulphides limited solubility prevails.

Vogt's views are only partially shared by C. Doelter, who thinks that the former is inclined to press the theories of physical chemistry in this new sphere further than is warranted in the present state of knowledge. This difference of opinion has led to a good deal of discussion,[1] but whatever view may be taken as to the arguments employed, there can be no doubt as to the interest aroused in the subject. Doelter's present position is set forth in a long paper communicated to the Viennese academy,[2] partly experimental and partly theoretical in char-

[1] See *Centr. Min.*, 1905, 144, 148, 361.

[2] *Sitzungsber. K. Akad. Wiss. Wien*, 1905, **114**, 529.

acter. On the experimental side, the paper deals with the viscosity of minerals in the neighbourhood of their melting points, which he has measured by observing the depths to which a platinum rod will penetrate the substance previously heated to a definite temperature. His results for the felspars confirm in the main the observations of Day and Allen, and he has also examined elæolite, leucite, diopside, augite, hedenbergite, and acmite. The melting point of a silicate is, he thinks, best defined as the point of transition from the crystalline to the amorphous condition, and he calls attention to the fact that this point is not necessarily identical with the point of liquefaction, which may be 100° or more above the transition point. The uncertainty as to what various authors have meant by the melting point when dealing with these substances is probably the cause of many of the discrepancies in the published values. Doelter further points out the necessity of distinguishing between the power of crystallisation possessed by a substance and the velocity with which it crystallises, and shows how the crystallising power may influence the order of separation of compounds from complex mixtures such as igneous rocks.

Constitution of the Zeolites.—The work of F. W. Clarke and of G. Steiger has shown that the bases in many zeolites can be replaced by ammonium when the minerals are heated with ammonium chloride in sealed tubes, and the latter[1] has lately found that on fusion with the nitrates of silver or thallium these elements can also be introduced into the silicate molecules. Thus, from analcite, $NaAlSi_2O_6,H_2O$, the compounds $AgAlSi_2O_6,H_2O$ and $TlAlSi_2O_6$ were prepared. In the case of chabazite and stilbite, the ratios of the substitution compounds were found to agree closely with the ratios 1 : 2 : 2 for the monoxide base, alumina, and silicic acid respectively, and, although in thomsonite incomplete substitution occurs, the ratios are nevertheless fairly well preserved. The experiments on chabazite proved of special interest, for the preparations were found to contain notable quantities of nitrate which could not be removed by washing. The compounds obtained from natrolite, scolecite, and mesolite indicate that all three minerals are derived from the trisilicic acid, $H_8Si_3O_{10}$.

A paper on the same subject has recently been published by F. W. Clarke.[2] It contains an account of some experiments on substitution by barium and strontium in the zeolites made by H. C. McNeil, as well as a theoretical discussion of the work of both McNeil and of Steiger. Analcite is shown to yield the compounds $BaAl_2Si_4O_{12}$ and $SrAl_2Si_4O_{12}$ as well as those mentioned above, and a sodium stilbite has also been prepared. In the case of chabazite, the action of barium chloride is to produce complete substitution, but it

[1] *Bull. U.S. Geol. Surv.*, 1905, **262**, 75.

[2] *Proc. Washington Acad. Sci.*, 1905, **7**, 257.

seems probable that a series of reactions takes place, the barium chabazite first formed being afterwards decomposed. Although the presence of chlorine and of NO_3 in substituted stilbite and chabazite can be explained on the assumption that chlorides or nitrates are occluded as such by the preparations, Clarke points out that it is possible that new compounds have been formed, analogous to sodalite or marialite, into which chlorine and NO_3 have entered as integral parts of the molecule. It may be mentioned here that experiments of a somewhat similar character on the action on kaolin of the chlorides of barium, strontium, sodium, and lithium have been made by Z. Weyberg.[1]

Water in Zeolites.—Very various opinions have been held as to the part played by water in zeolites. Some workers have regarded it as present partly as water of constitution, partly as water of crystallisation, and have constructed elaborate formulæ on the basis of this assumption. Others, basing their conclusions in the main on the continuous and reversible changes in the optical characters which take place when zeolites are heated, have held that water is in no way essential to the existence of these substances in the crystalline state, but that its part in the crystalline network is very much that of water held in the pores of a sponge. Others, again, have been inclined to regard zeolites as solid solutions. An important contribution to this subject, both from the experimental and from the theoretical side, has been made recently by F. Zambonini.[2] Using as material specimens of heulandite and of thomsonite of known composition, he has set himself to determine the phenomena of dehydration and reabsorption presented by these minerals under various conditions, and to trace the resulting changes in the optical properties. To this end he has determined at short intervals of time the loss of weight when the finely-powdered zeolites were dried: (1) over sulphuric acid in a vacuum at the ordinary temperature, (2) in a current of dry air at various temperatures, (3) in a current of moist air at various temperatures. He finds that over sulphuric acid a certain definite maximum loss is slowly attained. The process can be represented by a continuous curve, and in the case of a heulandite containing 16·6 per cent. of water the maximum loss amounted to 6·06 per cent. From a study of the dehydration curves obtained when currents of dry and moist air are respectively employed, he finds that moist air removes water more slowly than dry air. The difference in effect is apparently due to the tension of aqueous vapour present, and varies with the temperature. As regards reabsorption, he finds that the water given off over sulphuric acid or on exposure to a moderate degree of heat is rapidly

[1] *Centr. Min.*, 1905, 138, 646, 717.
[2] *Mem. R. Accad. Lincei*, 1905, **5**, 344.

taken up again when the zeolite is placed in moist air. If, however, the substance has been heated above a certain temperature, about 300° in the case of heulandite, the rate of reabsorption is much diminished and may be reduced to zero, even if the point of complete dehydration has not been attained. Further, he finds that above a certain temperature the duration of heating has a great retarding influence on the velocity of reabsorption when the substance is afterwards exposed to moisture. A similar effect is produced by a series of successive dehydrations if carried out at temperatures near that at which the diminution in the velocity of reabsorption begins. On the other hand, a series of successive dehydrations (followed by exposure to moisture) at moderate temperatures does not appear to influence the absorption or emission of water. A study of the optical characters of heulandite has shown that the mode of dehydration has an influence on the result. Cleavage flakes dehydrated by exposure to a temperature of 100° for from three to eight hours not only presented appearances different to those exhibited by flakes kept in a vacuum over sulphuric acid for twenty-four hours at the ordinary temperature, but always regained their original optical characters when exposed to moist air, which the latter failed to do. As the result of these experiments, Zambonini concludes that the view is untenable which regards the zeolites as hydrated salts, although they doubtless present many points of resemblance to such substances. Moreover, he believes that although the view that zeolites are solid solutions receives some support from their dehydration curves and from their optical behaviour, yet it fails to explain all the facts. He therefore prefers to regard them as analogous to the hydrogels studied by van Bemmelen, for, like the zeolites, the state of hydration of these substances depends on the temperature and on the concentration of the gaseous phase. Moreover, above a certain temperature the phenomena of dehydration are not reversible, and prolonged heating renders them incapable of reabsorbing water.

The dehydration of heulandite has also been studied by A. A. Ferro,[1] who used a specimen from Montecchio Maggiore. He determined the loss of weight experienced by the mineral when kept in a desiccator over calcium chloride and also when heated to various temperatures in air. Like Zambonini, he finds that the loss attains a maximum in both cases if sufficient time is allowed. When the mineral is kept in the desiccator, the maximum loss amounts to from 6·9 to 7·1 per cent., and can be quickly made good by exposure to moisture. Further, he points out that heulandite which has been kept in air absorbs water when exposed to a saturated atmosphere at a slightly elevated temperature, and loses it again when once more placed in air. Since

[1] *Atti R. Accad. Lincei*, 1905, **14**, ii, 140.

the water retained when equilibrium is reached, either over calcium chloride or on heating to 100—104°, amounts to approximately 3 mols., Ferro concludes that heulandite contains 3 molecules of water more intimately connected with the molecule than the rest, which may be termed hygroscopic water.

The Silicic Acids.—The importance of the preparation and study of the various silicic acids as an aid to our knowledge of the constitution of the naturally occurring silicates has lately been insisted on by E. Jordis[1] and by G. Tschermak.[2] While the former has occupied himself chiefly with the investigation of the conditions necessary for the preparation of pure silicic acid, the latter has attacked the problem from the mineralogical side. He points out that the silicates are probably salts of various acids derived from orthosilicic acid by removing from $n-1$ to $2n-1$ molecules of water from n molecules of H_4SiO_4. We thus obtain a series of acids such as H_4SiO_4, $H_6Si_2O_7$, $H_8Si_3O_{10}$, H_2SiO_3, $H_4Si_2O_6$, and so on. Some of these are polymerides, for example, $H_4Si_2O_6$ and H_2SiO_3; of others, isomerides can exist. If the natural silicates are salts of these acids, then on decomposing them with hydrochloric acid the corresponding silicic acid should be set free. To determine whether this is so or not, he proceeds as follows. A small quantity of the silicate is digested with hydrochloric acid at a temperature not exceeding 60° until decomposition is complete. This may take many days or even weeks. The silica obtained is washed by decantation until free from chlorine and then allowed to dry in the air in a weighed dish. The weight of the dish and contents is determined at intervals of twenty-four hours until it becomes constant, when the amount of silica present is found by igniting the residue. The results when plotted give the dehydration curve. On inspection, this is seen to consist of two parts, one portion corresponding to the drying process, the other to the decomposition of the silicic acid. The change in the course of the curve marks the point when dehydration is complete and decomposition is just beginning. It is difficult to determine the position of this point by direct observation or inspection of the curve, but it may be calculated with a fair degree of accuracy by means of observations taken on each side of it. Finally, as an aid to the better definition of the acids, their specific gravities were in some cases determined. The main results of the work are as follows. The acid obtained on decomposing silicon chloride by water is orthosilicic acid, H_4SiO_4 (sp. gr. 1·576). The same acid is obtained from natrolite, $Na_2H_4Al_2Si_3O_{12}$, and from dioptase, H_2CuSiO_4, which are accordingly acid salts of orthosilicic acid. Hemimorphite,

[1] *Zeit. anorg. Chem.*, 1905, **44**, 200.

[2] *Zeit. physikal. Chem.*, 1905, **53**, 349. See also an earlier paper on the same subject, *Sitzungsber. K. Akad. Wiss. Wien.*, 1903, **112**, i, 355.

$H_2Zn_2SiO_5$, behaves similarly, and is therefore also derived from orthosilicic acid. The application of the method to olivine yielded no certain result. From anorthite, $CaAl_2Si_2O_8$, metasilicic acid, H_2SiO_3 (sp. gr. 1·813), was obtained. Leucite, $KAlSi_2O_6$, yields a polymeride of metasilicic acid, $H_4Si_2O_6$, which differs from metasilicic acid in its appearance and also in its behaviour towards methylene-blue. A similar result was obtained with serpentine, which is therefore to be regarded as $H(Mg,OH)_3Si_2O_6$. From garnet, epidote, zoisite, and prehnite, the acid $H_4Si_3O_8$ (sp. gr. 1·910) was obtained. These minerals must therefore be regarded as silicoaluminates. Prehnite is the acid salt $Si_3O_8,Ca_2Al_2O_4,H_2$. In garnet, all the hydrogen is replaced by calcium, in epidote and zoisite its place is taken by the group AlOH. Albite, $NaAlSi_3O_8$, yields an acid, $H_2Si_3O_7$, which is stable when exposed to air.

In concluding this section, attention may be called to the "Treatise on Metamorphism," by C. R. van Hise, published as Memoir 47 of the United States Geological Survey towards the close of last year, which will be found to be a rich storehouse of information on many important branches of mineral chemistry. C. Doelter's work entitled "Physikalisch-chemische Mineralogie" (Leipzig: J. A. Barth, 1905) will also be found of value.

Artificial Formation of Minerals.

Diamond.—The study of the mode of occurrence of the diamonds found in the Cañon Diablo meteorite has led H. Moissan[1] to repeat some of his early experiments on the artificial formation of this substance, and to perform some new ones. Noticing that the diamonds were found in fissures which appeared to be connected with the presence of nodules containing sulphur, silicon, and phosphorus, he tried the effect of adding these elements to the molten iron from which carbon was to separate on cooling. The results showed that the presence of sulphur improved the yield. In the case of silicon, the yield also appeared to be improved, but the quality of the diamonds was poorer. The influence of phosphorus was unfavourable. His final conclusions may be summed up as follows: diamond is the variety of carbon which has been liquefied under high pressures; carbon heated to a high temperature under atmospheric pressure vaporises without becoming liquid and solidifies as graphite.

Similar ideas have guided W. Crookes[2] in some recent work on the same subject. He has pointed out that there is reason to believe that the physical constants of carbon are approximately as follows:

[1] *Ann. Chim. Phys.*, 1905, [viii], **5**, 174.
[2] *Proc. Roy. Soc.*, 1905, *A* **76**, 458.

boiling point, 3870° abs.; melting point, 4400°; critical temperature, 5800°; critical pressure, 2320 atmospheres. From these values the melting point pressure of 16·6 atmospheres can be calculated. If the diamond is the result of the crystallisation of liquid carbon, it is clear that pressure is an all important factor in its formation. Now as the experimental conditions for the simultaneous production of high temperatures and high pressures were realised in A. Noble's work on the explosion of cordite in closed cylinders, W. Crookes has examined the residues in the cylinders for diamonds, and his search has been rewarded by success.

C. V. Burton,[1] on the other hand, has suggested that carbon may crystallise as diamond under atmospheric pressure at temperatures lying between 550° and 700°. He has found that an alloy of lead with about 1 per cent. of calcium holds some carbon in solution. On passing steam over the alloy at a low red heat, no graphite was produced, but microscopic crystals were found in the residues, which from their shape, high refractive index, and chemical behaviour seemed to be diamonds. On performing the experiment at a full red heat, no such crystals could be detected, but graphite was obtained.

Ferron trite.—In the course of his work on the constitution and genesis of the native sulphates of iron, R. Scharizer [2] points out that ferronatrite, $Na_6Fe_2S_6O_{24},6H_2O$, and sideronatrite, $Na_4Fe_2S_4O_{17},7H_2O$, are probably both derived from $[(HO)Fe]_2[HSO_4]_4,6H_2O$, the acid ferric sulphate; thus sideronatrite is $[(HO)Fe]_2[NaSO_4]_4,6H_2O$ and ferronatrite is $[(NaSO_4)Fe]_2[NaSO_4]_4,6H_2O$. This view is confirmed by the fact that a substance having the composition of ferronatrite was obtained by mixing acid ferric sulphate and sodium hydrogen sulphate and allowing them to act on one another in the presence of moist air. Experiments on the production and transformation of sideronatrite support the constitution given above rather than that represented by the formula $2Na_2SO_4,Fe_2S_2O_9,7H_2O$.

Radioactive Minerals.

Several papers dealing with radioactivity and containing matter of mineralogical interest have appeared during the year. In the first place, R. J. Strutt [3] has described experiments made to determine the amounts of uranium, radium, thorium, and helium present in monazite, pitchblende, æschynite, gadolinite, and a number of other minerals. Uranium was estimated by the ordinary chemical methods, radium and thorium by means of their emanations, whilst helium was determined directly. The conclusions he arrives at are as follows: (1) the amount

[1] *Nature*, 1905, **72**, 397. [2] *Zeit. Kryst. Min.*, 1905, **41**, 209.
[3] *Proc. Roy. Soc.*, 1905, *A* **76**, 88.

of radium in a mineral is proportional to the uranium present. Incidentally he has shown that uranium occurs in some minerals, for example, monazite, not previously known to contain it. (2) Thorium is always accompanied by the uranium-radium combination, a fact which leads to the suggestion that thorium is producing uranium. (3) Helium only occurs in quantity if thorium is present, and is therefore probably produced more by thorium than by radium. (4) Thorium minerals vary much in emanating power. The conclusion that the amount of radium contained in a mineral is proportional to the uranium present has also been reached by B. B. Boltwood [1] after an examination of 22 samples belonging to 12 species of minerals containing from 0·3 to 74 per cent. of uranium. He believes that uranium is the parent of radium and that thorium has no part in its production; he has not, however, been able to obtain direct evidence of the change of uranium into radium. Like Strutt, he has detected uranium in monazite and, noticing the persistent occurrence of lead in these minerals, suggests that this element may result from the breaking up of uranium. He has followed up this idea in an important paper [2] on the ultimate disintegration product of the radioactive elements, in which he insists on the necessity of distinguishing between the primary minerals, which occur embedded in pegmatites and other rocks, and those of secondary origin, produced by the alteration of primary compounds or found in many mineral veins. To the first class belong the pitchblendes of Norway, North Carolina, Texas, and Connecticut, as well as æschynite, euxenite, fergusonite, samarskite, thorite, and thorianite. In the second class must be placed the pitchblendes of Cornwall, Saxony, and Bohemia, as well as gummite, autunite, and others. It is to the study of the composition of the primary minerals that we must look for evidence as to the existence of possible disintegration products. The secondary minerals may be too recent for the products to have accumulated in sufficient quantity for us to detect them. Studying the matter from this point of view, Boltwood finds that lead is present in all primary minerals which contain more than 2 per cent. of uranium. Further, since Hillebrand has found lead in all the uranium minerals he has analysed, Boltwood is confirmed in the view that lead is one of the final inactive disintegration products of uranium. The common association of uranium and thorium he interprets as supporting the idea that thorium is also a result of the disintegration of uranium: the opposite position to that adopted by Strutt. The small quantities of barium and of bismuth present in radioactive minerals are, he thinks, also to be attributed to disintegration, the former being possibly derived from actinium, the latter from thorium. The presence of hydrogen and of water in some of these

[1] *Phil. Mag.*, 1905, [vi], **9**, 599. [2] *Amer. J. Sci.*, 1905, [iv], **20**, 253.

minerals has long been a puzzle to mineralogists. It seems impossible to believe that water can have penetrated them from without, for many of them are compact enough to retain helium, and they are, moreover, often associated with anhydrous minerals such as apatite and magnetite. Boltwood points out that this difficulty vanishes if we admit that the hydrogen is also due to disintegration. The presence of argon is accounted for in the same way. Further, he shows that a comparison of a number of analyses of pitchblende made by Hillebrand reveals a rough proportionality between the amount of uranium and the amounts of lead, rare earths, and helium for specimens from the same general locality, and a closer relation between the quantities of UO_2 and of helium. For specimens from the same actual locality, the content of rare earths increases with the amount of lead present, and the proportion of helium, as compared with lead, is greatest in those which have the highest specific gravity. It should, however, be noted that the proportions of helium and of rare earths and lead are not the same in the pitchblendes of Connecticut and of Norway, the relative quantity of helium being smaller in the latter than in the former. This discrepancy may perhaps be explained by the greater geological age of the Norwegian pitchblendes. That helium and rare earths are absent from the secondary pitchblendes of Saxony and Bohemia is quite in accordance with theory. From a study of other minerals, Boltwood finds that the proportion of helium with respect to lead and uranium is high in dense compact substances of low emanating power, such as monazite and samarskite, and also in minerals such as thorianite found in the oldest geological formations, and that the minerals with the greatest proportion of thorium are in general the most hydrated. That monazite contains uranium has also been confirmed by F. Zerban,[1] who detected the element in all the monazite sands he examined, and also to the extent of 0·02 per cent. of U_3O_8 in a good crystal from Norway. In conclusion, we may mention that E. Rutherford and B. B. Boltwood[2] have found that the quantity of radium associated with 1 gram of uranium in a radioactive mineral is equal to $7{\cdot}4 \times 10^{-7}$ grams approximately. This result was arrived at by comparing the effect on an electroscope of the emanation from a radium bromide solution of known strength and from a specimen of pitchblende from Spruce Pine, North Carolina, containing 74·65 per cent. of uranium.

New Minerals.

Beckelite.—This mineral is a calcium cero-lanthano-didymo-silicate. It is found in brown grains, or in little isotropic octahedra or dodecahedra embedded in the albite of a dyke rock, consisting of

[1] *Ber.*, 1905, **38**, 557. [2] *Amer. J. Sci.*, 1905, [iv], **20**, 55.

albite and nepheline with magnetite and ægirine, which occurs in the elæolite syenite (mariupolite) of the Mariupol district on the sea of Azov. The cleavage is cubic, and the specific gravity 4·15 approximately. It is soluble in hot hydrochloric acid, and yields the following results on analysis :

SiO_2.	ZrO_2.	Al_2O_3.	Mn_2O_3.	$Yt_2O_3+Er_2O_3$.	Ce_2O_3.	La_2O_3.
17·13	2·50	0·30	0·07	2·80	28·10	13·60

Di_2O_3.	CaO.	K_2O.	Na_2O.	Ignition loss.	Total.
18·00	15·46	0·39	0·78	0·99	100·12

Traces of iron and magnesium were also detected. These numbers give the formula $Ca_3(Yt,Ce,La,Di)_4(Si,Zr)_3O_{15}$. J. Morozewicz,[1] the discoverer of the mineral, points out that by writing this in the form $Ca_3(Ce,La,Di)_2Si_3O_{12},(Ce,La,Di)_2O_3$ the analogy with the garnets is exhibited. It can also be written as follows : $CaR_2Si_2O_8,Ca_2SiO_4,R_2O_3$, where R = Ce,La,Di. The mineral may be distinguished from pyrochlore by its cleavage, lustre, and index of refraction, and also by the fact that it remains soluble in hydrochloric acid after ignition. It has been named in honour of Professor F. Becke.

Bowmanite is one of the many new minerals recently discovered by R. H. Solly[2] in the dolomite of the Binnenthal. Up to the present, only a few small, honey-yellow crystals have been found. They crystallise in the rhombohedral system, and have a perfect basal cleavage. Optical examination has shown that the mineral is pseudosymmetric. It appears to be essentially a phosphate of lime and alumina with small amounts of iron and water.

Doughtyite.—This name has been tentatively proposed by W. P. Headden[3] for a hydrated basic aluminium sulphate of the formula $Al_2(SO_4)_3,5Al_2(OH)_6,21H_2O$, found at Doughty Springs, Delta Co., Colorado.

Giorgiosite.—This name has been given by A. Lacroix[4] to a basic magnesium carbonate found as a fine powder composed of minute spherules on saline crusts obtained by Fouqué in 1866 from a fissure in the lava of Aphroëssa, Santorin. With it is associated a white, flocculent, isotropic material. The amount of these substances available was too small to admit of analyses being made, but as the properties of the latter are comparable with those of the freshly precipitated white magnesia of pharmacy, its composition is probably similar to that of hydromagnesite, $3MgCO_3,Mg(OH)_2,3H_2O$. The spherules appear to be identical with the product obtained when the precipitate

[1] *Bull. Acad. Sci. Cracovie*, 1905, année 1904, 485.
[2] *Min. Mag.*, 1905, **14**, 80.
[3] *Proc. Colorado Sci. Soc.*, 1905, **8**, 55.
[4] *Bull. Soc. franç. Min.*, 1905, **28**, 198. See also *Compt. rend.*, 1905, **140**, 1308.

of white magnesia is boiled for some time with its mother liquor. This product has been shown to be $4MgCO_3,Mg(OH)_2,4H_2O$, and this is accordingly the probable formula of the new mineral.

Hibschite occurs incrusting a green titaniferous melanite found in calcareous inclusions in the phonolite of the Marienberg near Aussig; it crystallises in isotropic octahedra. From two analyses, one of the melanite alone, the other of melanite mixed with hibschite, a formula has been arrived at by F. Cornu[1] identical with that of lawsonite, $H_4CaAl_2Si_2O_{10}$.

Hutchinsonite.—A few small crystals of this orthorhombic mineral, showing numerous faces and a good cleavage, have been obtained by R. H. Solly[2] from the dolomite of the Binnenthal. An analysis by G. T. Prior revealed the interesting fact that the substance is a thioarsenite of thallium, lead, silver, and copper containing nearly 20 per cent. of thallium.

Janosite.—A greenish-yellow efflorescence found on graphitic schist at the iron mine of Vashegy, Komitat Gömör, Hungary, has been analysed by H. Böckh and K. Emszt.[3] The substance, which is probably the result of the decomposition of pyrites, crystallises in minute, orthorhombic plates with good basal cleavage (sp. gr. = 2·51 to 2·548). The formula is $Fe_2(SO_4)_3,9H_2O$ and the mineral is therefore dimorphous with coquimbite (rhombohedral, sp. gr. 2·105) and closely allied to quenstedtite, $Fe_2(SO_4)_3,10H_2O$.

Kleinite.—A. Sachs[4] finds that small, yellow, hexagonal crystals from Terlingua, Texas, have the composition $3HgO,HgCl_2$. The mineral has a perfect basal cleavage. Its sp. gr. is 7·441.

Lengenbachite is a thioarsenite of lead with small amounts of silver, copper, and antimony, found by R. H. Solly[5] in thin, blade-shaped crystals in the dolomite quarry through which flows the Lengenbach, a tributary stream of the Binnenthal.

Marrite is another of the new minerals described by R. H. Solly[6] from the Binnenthal dolomite. Only a few small crystals have so far been found, and these belong to the oblique system and are very rich in faces. The chemical composition has not yet been determined.

Moissanite.—H. Moissan[7] found green, hexagonal crystals of carbon silicide together with the various forms of carbon in those residues from the solution of 53 kilograms of Cañon Diablo iron in hydrochloric acid which resisted the attack of hydrofluoric and sulphuric acids. A further study of these crystals[8] leaves no doubt as to their identity

[1] *Tsch. Min. Mitth.*, 1905, **24**, 327. [2] *Min. Mag.*, 1905, **14**, 72.
[3] *Föld. Közlöny*, 1905, **35**, 139.
[4] *Sitzungsber. K. Akad. Wiss. Berlin*, 1905, 1091.
[5] *Min. Mag.*, 1905, **14**, 78. [6] *Ibid.*, 76. [7] *Compt. rend.*, 1904, **139**, 773.
[8] *Compt. rend.*, 1905, **140**, 405. See also *Ann. Chim. Phys.*, 1905, [viii]. **5**, 174.

with carborundum, and G. F. Kunz, therefore, proposes that the naturally occurring compound should be called moissanite.

Paracelsian.—In the crystalline schists of Candoglia, Val del Toce, veins and nodules rich in quartz, diopside, calcite, pyrite, and other minerals are found together with calcareous fragments consisting almost entirely of calcite and pyroxene. Intimately associated with these veins and fragments occur pale yellow granules of a barium aluminium silicate. The optical properties and chemical composition of this mineral have been carefully studied by E. Tacconi,[1] whose analyses lead him to assign to it the formula $Ba_3Al_8Si_8O_{31}$. This suggests comparisons with barylite, $Ba_4Al_4Si_7O_{24}$, and celsian, $BaAl_2Si_2O_8$. From the former, it is clearly distinguished by its lower specific gravity, 3·325, that of barylite being 4·03, and from the latter by its very poor cleavage (celsian has two perfect cleavages and a sp. gr. 3·37). As, however, the optical characters of the mineral closely resemble those of celsian, Tacconi is doubtful whether it should be considered an entirely new species, and, therefore, following the suggestion of L. Brugnatelli, has named it paracelsian.

Purpurite occurs in small, irregular masses in the tin-bearing pegmatite and in the neighbouring schist at the Faires tin mine, King's Mountain, Gaston Co., North Carolina. It has also been observed on specimens from the lithium-bearing pegmatite dykes of Hiriart Hill, Pala, San Diego Co., California. The mineral has probably resulted from the oxidation of lithiophilite, the lithium being almost entirely removed and the iron and manganese oxidised and recrystallised with phosphoric acid and water. The mineral is of a rich deep red or reddish-purple colour, and appears to crystallise in the orthorhombic system. It is soluble in hydrochloric acid with evolution of chlorine, the iron and the manganese being present as ferric and manganic salts respectively. The following results were obtained on analysis:

Fe_2O_3.	Mn_2O_3.	P_2O_5.	H_2O.	CaO.	Na_2O.	Insol.	Total.
15·89	29·25	47·30	5·26	1·48	0·84	0·52	100·54

A trace of lithium was detected, and on heating to 105° the loss of water amounted to 3·31 per cent. Assuming the isomorphism of ferric and manganic oxides, L. C. Graton and W. T. Schaller[2] have deduced the formula $2(Mn,Fe)PO_4,H_2O$.

Smithite.—An analysis by G. T. Prior has shown that this mineral has the simple formula $AgAsS_2$. It was found by R. H. Solly[3] associated with other rare thioarsenites in the dolomite of the Binnenthal. The small red crystals exhibit numerous faces and belong to the oblique system.

[1] *Rend. Reale Istit. Lombardo*, 1905, [ii], **38**, 636.
[2] *Amer. J. Sci.*, 1905, [iv], **20**, 146. [3] *Min. Mag.*, 1905, **14**, 74.

Trechmannite also occurs in the Binnenthal dolomite.[1] Like hutchinsonite and smithite it is a red mineral, but from these the minute crystals may be distinguished by their symmetry, as they crystallise in the rhombohedral system. The composition of the mineral has not as yet been ascertained.

Stilpnochloran.—This substance has been discovered by F. Kretschmer[2] in the iron mines of Gobitschau, near Sternberg, Moravia. It is a product of the metamorphism of thuringite and occurs in shining yellow scales, thus suggesting the name, which is derived from στιλπνός, glittering, and χλωρός, yellow. It is decomposed by hydrochloric acid, and was found to have the following composition:

SiO_2.	Al_2O_3.	Fe_2O_3.	MnO.	CaO.	MgO.	P_2O_5.	H_2O.	Total.
33·30	4·37	44·33	0·34	1·22	1·73	0·37	14·10	99·76

These numbers lead to the formula $H_{24}(Al,Fe)_{10}(Ca,Mg)Si_9O_{46}$.

Tychite.—This exceedingly rare mineral occurs associated with northupite, $MgCO_3,Na_2CO_3,NaCl$, which it closely resembles in form and appearance, at the Borax Lake, San Bernardino Co., California. It was discovered by the chance that a small octahedron selected for examination from a parcel of northupites failed to react for chlorine, but was found to contain sulphate. Following up this observation, S. L. Penfield and G. S. Jamieson[3] tested some thousands of northupites, but were only able to detect three more crystals of the new mineral. Its accidental discovery finds expression in the name tychite, from τύχη, luck. Thinking that the composition of the mineral might resemble that of northupite, Penfield and Jamieson attempted to prepare it artificially. In this they were successful, for on adding magnesium sulphate to a solution of the carbonate and sulphate of sodium, and heating the mixture for five days on a steam-bath, a crystalline precipitate was obtained. The physical characters of the precipitate agreed with those of the natural crystals, and as its composition was found to be $2MgCO_3,2Na_2CO_3,Na_2SO_4$, this is probably the formula to be assigned to tychite. Penfield and Jamieson further point out that northupite and tychite both take some time to form when their constituents are brought together in solution, and that whereas the former is readily decomposed by boiling water, the latter is almost insoluble. This behaviour suggests that these substances probably possess a complex molecular structure which may perhaps find expression in a constitutional formula in which four carbon atoms are joined with four oxygen atoms to form a ring. The isomorphism of the two compounds can only be accounted for by the mass effect of the large number of sodium, oxygen, carbon, and magnesium atoms, which overpowers the morpho-

[1] *Min. Mag.*, 1905, **14**, 75. [2] *Centr. Min.*, 1905, 203.
[3] *Amer. J. Sci.*, 1905, [iv], **20**, 217.

tropic influence of either the two chlorine atoms or the sulphate group.

A New Zeolite.—In the pegmatite veins of the granite of San Piero in Campo, Elba, small, eight-sided crystals occur which G. D'Achiardi [1] thinks may perhaps be a new species of zeolite. He finds that the crystals are complex twins and that they have the following composition :

SiO_2.	Al_2O_3.	CaO.	SrO.	MgO.	K_2O.	Na_2O.	H_2O.	Total.
61·41	11·15	5·52	1·14	trace	3·31	2·06	13·51	98·10

These percentages do not quite accord with those given by any known zeolite, although they resemble to some extent those of some heulandites in spite of a considerable difference in the amounts of alumina and alkaline oxides. The two minerals, however, differ widely in habit. D'Achiardi deduces the following formula from his results : $(Na_2,K_2,Ca)_3Al_4Si_{18}O_{45},14H_2O$.

Mineral Analyses.

Many mineral analyses have been published during the year. Of these, some have thrown light on the composition of rare and imperfectly described species and varieties, others, although referring to well-known minerals, are interesting because the determination of the chemical composition has been accompanied by a careful study of the crystallography and optical characters of the material analysed. The most important of these investigations will be given below under the name of each species arranged alphabetically.

Amphibole Group.—An analysis of the *amphibole* from the syenite of Biella has already been published by Cossa. It is remarkable as showing a high percentage of ferric oxide and alumina and little magnesia, resembling in this respect the analysis made by Flink of so-called diastatite from Nordmarken. F. Zambonini,[2] who has lately made an elaborate study of the minerals of the Biella syenite, has re-examined the amphibole, and his numbers, which differ a good deal from those obtained by Cossa, are given below :

SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	CaO.	MgO.	K_2O.	Na_2O.	H_2O.	Total.
51·32	0·84	6·11	3·28	7·39	trace	13·59	16·17	0·36	0·91	0·30	100·27

Zambonini represents the substance as composed of the following molecules : $5Mg_2Al_4Si_2O_{12}$; $3FeFe_2Si_4O_{12}$; $2(Na_2,K_2,H_2)_4Si_4O_{12}$; $32(Mg,Ca)_4Si_4O_{12}$; $5Fe_4Si_4O_{12}$, and points out that the composition cannot be satisfactorily explained on Scharizer's view that amphibole is xCa$(Mg,Fe)_3Si_4O_{12},y(R'_2R'')_3R'''_2Si_3O_{12}$, because it contains too much silica. The geometrical constants also differ considerably from

[1] *Proc. Verb. Soc. Toscana Sci. Nat.*, 1905, Jan. 15.
[2] *Zeit. Kryst. Min.*, 1905, **40**, 231.

those of other amphiboles and fail to support the view expressed by Brögger that the angle β increases with the amount of iron and manganese present. A specimen of the rather rare variety of hornblende called *edenite*, which contains much alumina, but little or no ferric oxide, has been analysed by A. Roccati [1] with the following results:

SiO_2.	Al_2O_3.	Fe_2O_3.	MgO.	CaO.	$Na_2O + K_2O$.	Ignition.	Total.
49·25	13·82	trace	20·95	11·91	2·80	0·91	99·64

The composition may be expressed by the formula

$$6(R'',R'_2)O,Al_2O_3,6SiO_2.$$

The mineral is found as grains and crystals embedded in limestones associated with the gneissic rocks of Piano dei Chiotas, in the Maritime Alps.

A well developed crystal of *black hornblende* from Lukow, Bohemia, shown by microscopic examination to be free from inclusions, has been analysed by F. Hanusch at the request of J. E. Hibsch.[2] The results are as follows:

SiO_2.	TiO_2.	F.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	CaO.
39·60	2·50	0·10	18·51	5·50	2·26	0·74	12·57

MgO.	K_2O.	Na_2O.	H_2O.	CO_2.	Total.
14·11	1·87	2·58	0·26	0·07	100·67

Aragotite.—H. G. Hanks [3] has examined a specimen of this rare hydrocarbon from the Aetna quicksilver mine, Napa Co., California. On analysis, E. Huetlin found 88·10 per cent. of carbon and 9·17 per cent. of hydrogen.

Ardennite.—This silicate is interesting because it contains arsenic and vanadium. As the formula hitherto assigned to it is very complicated, and as the state of oxidation of the vanadium has never been satisfactorily made out, W. Prandtl [4] has investigated the substance afresh. He concludes that arsenic and vanadium are both present in the quinquevalent state, and writes the formula

$$10SiO_2,(As,V)_2O_5,5(Al,Fe)_2O_3,10(Mn,Mg,Ca,Fe)O,6H_2O,$$

basing it on the following analytical data:

SiO_2.	As_2O_5.	V_2O_5.	Al_2O_3.	Fe_2O_3.	MnO.	MgO.	CaO.	FeO.	H_2O.	Total.
27·77	9·91	0·81	25·25	0·53	22·70	5·20	1·44	0·65	5·24	99·50

Atopite has been found in small, yellow octahedra on manganese ores from the mines of Miguel Burnier, Minas Geraes, Brazil. It has been examined by E. Hussak,[5] who finds that its formula is $(Ca,Mn,Na_2)_2Sb_2O_7$, like that of the specimens from Långban, in Sweden.

Awaruite.—The naturally occurring alloys of iron and nickel have

[1] *Revista Min.*, 1905, **32**, 12.
[2] *Tsch. Min. Mitth.*, 1905, **24**, 271.
[3] *J. Roy. Micros. Soc.*, 1905, 673.
[4] *Zeit. Kryst. Min.*, 1905, **40**, 392.
[5] *Centr. Min.*, 1905, 240.

been the subject of investigations by G. C. Hoffmann[1] and by G. S. Jamieson.[2] The former has given the name souesite to a specimen found in the auriferous gravels of the Fraser River, British Columbia. The latter has examined material from Josephine County, Oregon, and from the Smith River, California. On comparing his results with those of Hoffmann, as well as with the published data for similar material from Awarua Bay, New Zealand, from the Elvo River, Piedmont, and from Josephine County (so-called josephinite), Jamieson finds that this alloy has not a definite composition, the amount of nickel varying from 67·63 per cent. up to 77·17 per cent. He therefore rightly deprecates the use of the names josephinite and souesite, and urges that the name awaruite should be alone retained.

Blende.—C. Rimatori[3] has continued his quantitative and spectroscopic investigation of Sardinian blendes. Fifteen specimens were examined, and cadmium found in all up to a maximum of 1·23 per cent. Copper was present in several, bismuth in two. Seven belonged to the variety called marmatite, and one of these contained 5·81 per cent. of manganese, the largest quantity hitherto reported. Two contained both gallium and indium and six others indium alone; in one of these, 0·0243 per cent. of indium was found.

Californite.—This name was given by G. F. Kunz to a remarkable compact variety of vesuvianite found in Siskiyou Co., California. Similar material was subsequently obtained from Fresno Co., California.

The analytical data have been interpreted by F. W. Clarke and G. Steiger[4] as leading to the approximate empirical formula $2H_2O,2Al_2O_3,7CaO,6SiO_2$ or $Al_2Ca_7(SiO_4)_6(AlOH)(AlO_2H_2)H$. If part of the water is extraneous, the following much simpler formula may hold: $Al_2Ca_7(SiO_4)_6(AlOH)_2$, and this fairly represents a good many other analyses of vesuvianite. Clarke and Steiger further point out that while $Al_2Ca_6(SiO_4)_5(AlOH)$ is a good expression for the average composition of the species it does not fit the extremes, and from a study of more than forty analyses they suspect that vesuvianite is a mixture of the four following molecules: $Al_2Ca_7(SiO_4)_6(AlOH)_2$; $Al_2Ca_7(SiO_4)_6(AlO_2H_2)_4$; $Al_2Ca_7(SiO_4)_6H_4$; $Al_2Ca_7(SiO_4)_6Ca_2$, the first and third usually predominating. About one-seventh of the calcium is replaced by magnesium, and in wiluite the group BOH probably occurs.

Carnotite.—This radioactive uranium mineral has been tested for helium by E. P. Adams.[5] As he failed to find any, he concluded that

[1] *Amer. J. Sci.*, 1905, [iv], **19**, 319.
[2] *Ibid.*, 1905, [iv], **19**, 413.
[3] *Atti R. Accad. Lincei*, 1905, **14**, i, 688.
[4] *Bull U.S. Geol. Surv.*, 1905, **262**, 72.
[5] *Amer. J. Sci.*, 1905, [iv], **19**, 321.

helium, if ever present, had escaped owing to the permeable character of the mineral.

Chrysoberyl.—A crystal from Maskinonge Co., Quebec, has been analysed by N. N. Evans[1] with the following results:

BeO.	Al_2O_3.	Fe_2O_3.	Total.	Sp. gr.
17·78	76·76	6·07	100·61	3·52

Some if not all the iron was probably present as FeO; no calcium or magnesium were found.

Columbite.—W. P. Headden[2] has analysed specimens of this mineral (I) from Cañon City, Colorado, and (II) from Black Hills, South Dakota, with the following results:

	Cb_2O_5.	Ta_2O_5.	WO_3.	SnO_2.	FeO.	MnO.	Ignition.	Total.
I.	56·48	22·12	0·45	0·11	8·07	12·45	0·15	99·83.
II.	54·64	25·62	—	0·15	6·80	12·61	—	99·82.

Copper-pitch Ore.—A dark brown, pitch-like mineral from Amzalar, Roumania, has been analysed by Th. Nicolau.[3] The theory that copper-pitch ore is a mixture of chrysocolla and limonite is not supported by the results, and although no simple formula can be calculated the mineral must be regarded as homogeneous, a conclusion already reached by Lindgren and Hillebrand.

Dognacskaite.—The composition of this bismuth copper sulphide has hitherto rested on an analysis by Maderspach. At the request of A. Otto, an analysis has been published by Koechlin[4] showing a much smaller quantity of bismuth, corresponding to the formula of wittichenite, $Bi_2S_3,3Cu_2S$. As, however, the specific gravity of dognacskaite is 6·79 to 6·72 and that of wittichenite is 5, and as, moreover, the former mineral has a good cleavage and the latter nono, F. Neugebauer[5] has made a fresh analysis of carefully selected material. From his results, he deduces the formula $Bi_4Cu_2S_7$ or $2Bi_2S_3,Cu_2S$, and thinks that the individuality of dognacskaite as a species may be considered to be established.

Dumortierite has been the subject of an elaborate investigation by W. T. Schaller,[6] who has not only collected the results of other workers, but has determined the crystallographic and optical properties of the mineral, and made three very careful analyses. The results of these are given below; I and II refer to a specimen from near Dehesa, San Diego Co., California, III to material from Skamania Co., Washington.

[1] *Amer. J. Sci.*, 1905, [iv], **19**, 316.
[2] *Proc. Colorado Sci. Soc.*, 1905, **8**, 55.
[3] *Ann. Sci. Univ. Jassy*, 1905, **3**, 103.
[4] *Tsch. Min. Mitth.*, 1905, **24**, 117.
[5] *Tsch. Min. Mitth.*, 1905, **24**, 323.
[6] *Amer. J. Sci.*, 1905, [iv], **19**, 211; see also *Bull. U.S. Geol. Surv.*, 1905, **262**, 91.

	SiO_2.	Al_2O_3.	Ti_2O_3.	Fe_2O_3.	H_2O.	B_2O_3.	Total.
I.	28·58	63·31	1·49	0·21	1·53	5·21	100·33
II.	28·78	63·30	1·40	0·25	1·51	5·53	100·77
III.	28·51	59·75	0·95*	2·48	2·12	5·54	100·03

* Titanium calculated as TiO_2 ; 0·68 CaO also present.

The first two analyses agree exceedingly well with the formula $8Al_2O_3,B_2O_3,H_2O,6SiO_2$. In the case of the third, the agreement is not quite so close, but this analysis is of less value than the other two as the material was known to be contaminated with andalusite and titanite (leucoxene) as well as with traces of pyrite. Schaller points out that an analysis by Ford of a specimen from Arizona is completely in accord with his formula, although Ford's results for the Californian and New York minerals are less perfectly in harmony with it: the same is true for the analyses made by Whitfield and Riggs. By writing the formula thus, $(SiO_4)_3Al(AlO)_7(BO)H$, its analogy with andalusite is exhibited, and its alteration into muscovite explained.

Enargite.—The following is an analysis by W. P. Headden[1] of crystalline enargite from the Powers Mine, Willis Gulch, Gilpin Co., Colorado:

S.	As.	Sb.	Cu.	Pb.	Fe.	Zn.	Total.
29·35	16·17	3·77	48·40	1·83	0·30	0·19	100·01

Epidote.—The crystallographic, optical, and chemical properties of good crystals of epidote from Inverness-shire have been carefully studied by H. H. Thomas and W. Pollard.[2] The mineral is an interesting member of the epidotes with a low percentage of ferric iron, and falls naturally into the series. In composition, it is very similar to the epidotes from Huntington, Mass., the Zillerthal, and Val Maigels. Its formula is $Ca_4Al_4(AlOH)_2(SiO_4)_6$.

Felspar Group.—In addition to the important investigation of Day and Allen referred to above, we may note the following points. G. Melczer[3] has determined with great care the crystallographic constants of an *albite* from Nadabula, shown by qualitative examination to be pure. He finds $a:b:c = 0{\cdot}6350:1:0{\cdot}5578$; $\alpha = 94°6'$, $\beta = 116°36\frac{1}{3}'$, $\gamma = 87°52'$. The extinction on 010 is 20°30′, on the base 3°5′ to 4°30′.

An *albite* from Nurra, Sardinia, has been examined by C. Viola,[4] and an analysis made by H. Steinmetz (I, below). Viola thinks that the lime is due to impurities and regards the mineral as a mixture of 10 molecules of albite with 1·3 molecules of orthoclase. He has determined the

[1] *Proc. Colorado Sci. Soc.*, 1905, **8**, 55.
[2] *Min. Mag.*, 1905, **14**, 109.
[3] *Zeit. Kryst. Min.*, 1905, **40**, 571.
[4] *Boll. R. Com. Geol. d'Italia*, 1905, [iv], **6**, 106.

indices of refraction and the extinctions and finds that, whilst the former indicate a nearly pure albite, the latter belong rather to an oligoclase-albite. An *orthoclase* from Biella, geometrically and optically normal, has been analysed by F. Zambonini.[1] Some very pure white crystals gave the results quoted under II below. At the same locality occur crystals of *oligoclase*. Zambonini has also measured these, and finds that their constants are the same as those of the Vesuvian oligoclase determined by vom Rath; he quotes an analysis by C. Montemartini (III, below), and points out that on Tschermak's theory the mineral consists of 7Ab + 3An.

	SiO_2.	P_2O_5.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	K_2O.	Na_2O.	Ignition.	Total.
I.	67·16	—	17·57	—	4·52	—	1·07	9·51	—	99·83
II.	64·61	trace	18·75	trace	0·83	trace	14·46	0·81	—	99·46
III.	63·51	—	22·40	—	3·38	0·08	1·24	8·66	0·48	99·75

Fibroferrite.—W. P. Headden[2] has found that aggregates of greenish-white, acicular crystals from Green River, Utah, have the formula $Fe_2O_3,2SO_3,10H_2O$.

Fiedlerite is an oxychloride of lead found in ancient slags at Laurion. A. de Schulten[3] has recently determined its composition to be $PbO,2PbCl_2,H_2O$. It is therefore related to penfieldite, $PbO,2PbCl_2$, and to laurionite, $PbO,PbCl_2,H_2O$, which both occur at the same locality.

Glaucodote is found in imperfect crystals at the Standard Consolidated gold mine, Sumpter, Oregon. A crystal has been measured, and the material analysed by W. T. Schaller.[4] As the ratio of cobalt to iron is approximately 3 to 2, the formula may be written $Co_3Fe_2As_5S_5$.

Gyrolite occurs with pectolite and datolite at Fort Point, San Francisco. W. T. Schaller[5] has analysed the material and deduces the formula $5H_2O,4CaO,6SiO_2$, thus confirming the view taken by F. W. Clarke. The mineral is probably oblique and related to heulandite.

Huebnerite.—W. H. Hobbs[6] has published the following analysis by S. V. Peppel of a nearly pure huebnerite, $MnWO_4$, found in large brown crystals at Dragoon Summit, Arizona.

SiO_2.	WO_3.	MnO.	FeO.	Total.
1·10	75·10	22·87	0·81	99·88

Kentrolite.—Specimens of this rare mineral have recently been discovered by D. Lovisato,[7] near Ozieri, Sardinia, where it occurs in

[1] *Zeit. Kryst. Min.*, 1905, **40**, 251.
[2] *Proc. Colorado Sci. Soc.*, 1905, **8**, 55.
[3] *Compt. rend.*, 1905, **140**, 315.
[4] *Bull. U.S. Geol. Surv.*, 1905, **262**, 132.
[5] *Ibid.*, 124.
[6] *Amer. Geol.*, 1905, **36**, 179.
[7] *Atti R. Accad. Lincei*, 1905, **14**, i, 696.

little brownish-red spherules and aggregates. An analysis by C. Rimatori gave the following results:

SiO_2.	PbO.	CuO.	Fe_2O_3.	MnO_2.	CaO.	MgO.	H_2O.	Total.
17·71	60·02	trace	1·55	18·87	0·33	trace	1·79	100·27

In composition, the Sardinian mineral somewhat resembles that from Långban, but in its appearance and mode of occurrence it is more like the specimens from Chili.

Melilite.—The study of a slag has led F. Zambonini[1] to analyse melilite from Capo di Bove, and to criticise the formulæ proposed for this mineral. His results agree closely with those already published by Damour. Very various views as to the nature of melilite have been maintained, thus Des Cloizeaux has calculated the formula $12R''O,2R'''_2O_3,9SiO_2$, and Groth has arrived at a somewhat similar expression, $(Ca,Mg)_6(Al,Fe)_2Si_5O_{19}$. Vogt, on the other hand, regards melilite as an isomorphous mixture of gehlenite, $R''_3R'''_2Si_2O_{10}$, with åkermanite, an artificial substance of the formula $R''_4Si_3O_{10}$. Bodländer, however, has pointed out as a necessary consequence of Vogt's view that the ratio of the oxygen in the silica to that present as R″O must vary between the limits 1·33 and 1·5. Discussing his own analyses and those of others in the light of Bodländer's criticism, Zambonini finds that this ratio is always much smaller than that required by Vogt's hypothesis. If, however, it is assumed that the alumina and ferric oxide are present as gehlenite and the corresponding quantity of this mineral is subtracted, Zambonini finds that silica and oxides of the type R″O are always present in the exact proportions required to form a metasilicate. Melilite may accordingly be regarded as a mixture of gehlenite, $R''_3R'''_2Si_2O_{10}$, with n molecules of a metasilicate, $R''SiO_3$. It may also be represented as an isomorphous mixture of $R''SiO_3$ with an aluminate of the type $R''R'''O_4$; this is the view held by Bodländer and preferred by Zambonini. A third possibility is to write it $R''R'''_2Si_2O_8,nR''_2SiO_4$. If this last expression is adopted, Des Cloizeaux's formula becomes

$$2R''R'''_2Si_2O_8,5R''_2SiO_4.$$

Olivine.—The investigation of a gabbro containing both olivine and a rhombic pyroxene suggested that it would be interesting to determine the relative proportions of the iron and magnesium compounds present in these two minerals when they occur together. J. Schiller[2] has therefore analysed the olivine and the bronzite from bombs found at Kapfenstein, near Gleichenberg.

The olivine consists of 90·2 per cent. of Mg_2SiO_4 and 9·8 per cent. of Fe_2SiO_4. If, in working out the results for the bronzite, the water, lime, and titanium oxide present are omitted, and ferrous oxide and

[1] *Zeit. Kryst. Min.*, 1905, **41**, 226. [2] *Tsch. Min. Mitth.*, 1905, **24**, 309.

magnesia considered as equivalent, we arrive at the following composition: 86 per cent. of $Mg_2Si_2O_6$, 3·9 per cent. of $MgAl_2SiO_6$, 3·2 per cent. of $MgFe_2SiO_6$, and 6·9 per cent. of $Fe_2Si_2O_6$. Here also the ferrous silicate and the magnesium silicate are in the ratio 1 : 9. There is, therefore, no essential difference between the proportions in which the ferrous compounds and the magnesium compounds occur in the two minerals. A consideration of the work of others leads Schiller to conclude that when olivine and rhombic pyroxene occur together in rocks free from felspar, the ferrous and magnesium compounds exist in about the same molecular ratio in each. When, on the other hand, they occur in rocks which contain felspar, the olivine is always the richer in the magnesium compound.

Prehnite.—Specimens from Lower California and from Biella have been analysed by W. T. Schaller [1] and by F. Zambonini [2] respectively. In both cases, the composition is well expressed by the formula $H_2Ca_2Al_2Si_3O_{12}$.

Pyroxene Group.—The optical characters of good crystals of *diopside* from the eozoon limestone of Côte St. Pierre, Canada, have been described by H. Preiswerk.[3] The mineral has been analysed by F. Hinden, and may be regarded as a compound of 96·25 per cent. of $CaMgSi_2O_6$, 1·92 per cent. of $FeMgSi_2O_6$, 1·51 per cent. of $MgAl_2SiO_6$, and 0·32 per cent. of $MgFe_2SiO_6$, although the actual numbers obtained show an excess of basic oxides as compared with silica (I below).

Crystals of *black augite* from Canale Monterano, near Rome, have been measured and analysed by F. Zambonini;[4] his results are given under II below.

	SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	CaO.	MgO.	Na_2O.	H_2O.	Total.
I.	53·70	—	0·95	0·32	0·65	—	25·45	19·04	—	0·47*	100·58
II.	50·88	1·02	5·36	1·21	4·67	trace	22·96	13·78	0·50	0·34	100·72

* Ignition loss.

Tengerite.—In an account of the locality at Barringer Hill, Llano Co., Texas, from which have come fine specimens of many rare radioactive minerals, W. E. Hidden [5] has described the occurrence in gadolinite of white, semi-globular concretions which may perhaps be tengerite. As the composition of this species had not previously been determined, the following analysis was made by W. F. Hillebrand:

Yt group.	Ce group.	Fe_2O_3.	BeO.	CO_2.	$H_2O > 105°$.	$H_2O < 105°$.	SiO_2.	MgO
40·8	7·0	4·0	9·7	19·6	14·1	3·2	0·4	1·2*

* Includes alkalis and loss.

No definite formula can be calculated, but the presence of glucinum

[1] *Bull. U.S. Geol. Surv.*, 1905, **262**, 128. [2] *Zeit. Kryst. Min.*, 1905, **40**, 262.
[3] *Ibid.*, 498. [4] *Ibid.*, 52. [5] *Amer. J. Sci.*, 1905, [iv], **19**, 429.

in the form of carbonate is remarkable, and may perhaps indicate the existence of a new glucinum mineral mechanically mixed with a basic hydrous carbonate of the rare earths of the yttrium group.

Tetradymite.—The composition of cleavage masses of this mineral from Whitehorn, Fremont Co., Colorado, has been found by W. F. Hillebrand [1] to agree well with the formula Bi_2Te_3. In this connection, we may notice that K. Mönkemeyer [2] has made a careful study of the cooling curves of mixtures of bismuth and tellurium taken in various proportions. These experiments lead to the conclusion that Bi_2Te_3 is the only compound of the two elements which can exist, and this view was confirmed by a study of the sections cut from the solidified masses.

Thorianite.—The leading characteristics of this interesting mineral were given last year; a more detailed description has recently been published by W. R. Dunstan and G. S. Blake,[3] who give the following analysis:

ThO_2.	UO_2.	UO_3.	CeO_2.	PbO.	Fe_2O_3.	CaO.	He.	Insol.	Total.
78·86	6·03	9·07	1·02	2·59	0·46	1·13	0·39	0·20	99·75

The number quoted for helium was calculated on the assumption that the whole of the gas evolved from the mineral consisted of that element. Lanthanum and didymium are included under cerium. A trace of phosphate was detected. This analysis differs somewhat from those previously published. Taken together, they show that the mineral consists essentially of thoria, oxide of uranium, and varying quantities of ceria. The exact part played by the uranium cannot be said to be as yet precisely made out. Possibly it was originally all present as UO_2, in isomorphous admixture with the thoria. Thorianite is slightly less radioactive than pitchblende, a mineral with which it is evidently closely related. From the residues left after fusing about 250 kilograms of thorianite with potassium hydrogen sulphate, O. Hahn [4] has isolated a highly radioactive product differing markedly from radium. The rate of decay of the emanation from this substance was found to be identical with that of the thorium emanation. Further work [5] has led Hahn to the conclusion that a new element, "radiothorium," is contained in these residues.

Thuringite.—In last year's report, reference was made to Zalinski's work on thuringite. Attention may now be called to F. Kretschmer's [6] observations on specimens from the iron mines of Gobitschau, where it occurs associated with its decomposition products limonite and the new mineral stilpnochloran. An analysis by S. Vogl shows that it is very similar to the thuringite from Zirmsee,

[1] *Bull. U.S. Geol. Surv.*, 1905, **262**, 57.
[2] *Zeit. anorg. Chem.*, 1905, **46**, 415.
[3] *Proc. Roy. Soc.*, 1905, series A, **76**, 253.
[4] *Ibid.*, 115.
[5] *Ber.*, 1905, **38**, 3371.
[6] *Centr. Min.*, 1905, 195.

and if Tschermak's theory of the composition of the mineral is accepted it may be expressed as consisting of 4 molecules of amesite with 3 molecules of strigovite.

Titanite.—In spite of much analytical work, the composition of this mineral still offers difficulties. Attention has been called to some of these by F. Zambonini[1] in the course of his work on the minerals of Biella. At this locality, titanite occurs in good crystals which were measured and in grains which were found to resemble in composition the variety described by Groth from the Plauen Grund. No satisfactory formula could, however, be deduced from the following analytical data:

SiO_2.	TiO_2.	Fe_2O_3.	FeO.	Al_2O_3.	$(Yt,Ce)_2O_3$.	MnO.	CaO.	MgO.	H_2O.	Total.
30·89	30·58	5·77	trace	2·81	3·07	0·40	26·09	0·25	0·86	100·72

The ordinarily accepted formula, $CaTiSiO_5$, also fails to represent the composition of the dark brown crystals from Urotva, Transylvania, described by Th. Nicholau,[2] who has published the two following analyses:

TiO_2.	SiO_2.	CaO.	MnO.	Al_2O_3.	Na_2O.	Total.
42·24	31·10	24·30	2·09	0·64	0·06	100·43
42·65	31·03	24·19	2·34	0·55	trace	100·76

Zeolite Group.—A specimen of *heulandite* from the Biella syenite has been found by Zambonini[3] to contain considerably less silica and more alumina than is usual in this mineral. Its formula is $Ca_2Al_4Si_9O_{26},10H_2O$. Zambonini[4] has also examined the *chabazite* from the same locality, and points out that it too has an abnormal composition, being exceptionally rich in lime and poor in alkalis. The analytical numbers do not support Streng's hypothesis that the chabazites are mixtures of $CaAl_2Si_6O_{16},8H_2O$ with $CaAl_2Si_2O_8,4H_2O$. Chabazite has also been analysed by A. Bygdén.[5] The two specimens examined came from Gellivare, Malmberg. The first may be approximately represented by the formula $RO,Al_2O_3,4SiO_2,6H_2O$, the second by $2RO,2Al_2O_3,9SiO_2,13H_2O$. To *stilbite* from the same locality, Bygdén assigns the formula $2RO,2Al_2O_3,13SiO_2,14H_2O$.

In concluding this section, we may notice that J. Schilling[6] has compiled a useful table showing the specific gravities, percentages of tantalum and of niobium and the localities of all the minerals containing tantalum of which analyses have as yet been published.

[1] *Zeit. Kryst. Min.*, 1905, **40**, 239. [2] *Ann. Sci. Univ. Jassy*, 1905, **3**, 169.
[3] *Zeit. Kryst. Min.*, 1905, **40**, 266. [4] *Loc. cit.*, 263.
[5] *Bull. Geol. Instit. Univ. Upsala*, 1905 (for 1902—1903), **6**, 92.
[6] *Zeit. angew. Chem.*, 1905, **18**, 883.

Meteorites.

The death of Professor E. Cohen in the early part of the year has removed from this field of inquiry one of its most active cultivators. Among the latest of his publications [1] may be noticed a catalogue of the meteorites in the collection at Greifswald. A catalogue by G. Dewalque [2] of the meteorites preserved at Ghent, Gembloux, Liége, Louvain, and Maredsous is also worthy of mention.

The work on meteorites of most general interest which has recently appeared is contained in a paper by F. Rinne,[3] in which the composition and structure of meteoric iron are compared with those of iron and steel, the subject being treated from the point of view of physical chemistry and the phase rule. The paper opens with a very lucid description of the phenomena of solidification presented by cast iron and steel, and of the composition and mutual relations of ferrite, martensite, cementite, and pearlite. The changes which may occur after the metal has solidified are set forth with equal clearness. Having called attention to the fact that the meteoric irons contain compounds similar to those found in technical iron, Rinne points out that far-reaching transformations may take place in meteorites long after the alloy composing them has become solid. Thus, nickel-iron is the equivalent of ferrite, cohenite $(Fe,Ni,Co)_3C$ of cementite Fe_3C, schreibersite (rhabdite) of Fe_3P, troilite of FeS, and just as martensite may break up on cooling into ferrite and the mixture of ferrite and cementite known as pearlite, so also in nickel-iron similar changes may occur. Now, iron and nickel being closely related elements, they may be expected to form mixed crystals, and there is reason to believe that their behaviour on solidification can be represented by a curve of the second type of Bakhuis Roozeboom's classification. The study [4] of the magnetic and other physical properties of the alloy leads to the conclusion that on further cooling differentiation of the solid takes place into crystals rich in iron and crystals rich in nickel, the series being interrupted by a gap or lacuna, the differentiation following a course which can be represented by a curve of Bakhuis Roozeboom's fifth type. A chemical compound of iron and nickel may also possibly exist. A study of this curve leads to the following classification of the alloys of nickel and iron : (1) group below the lacuna. This includes alloys containing up to 7 per cent. of nickel, and to these the name kamacite has been given. (2) Group of the lacuna. In this group

[1] *Mitth. naturwiss. Ver. Neu-Vorpommern und Rügen*, 1905, **36**, (1904), 1.
[2] *Ann. Soc. Géol. Belg.*, 1905, **32**, M 15.
[3] *Neues Jahrb. Min.*, 1905, i, 122.
[4] Compare F. Osmond and G. Cartaud, *Compt. rend.*, 1903, **137**, 1057.

three sub-classes may be distinguished: (*a*) kamacite is crystallised with the eutropic mixture of kamacite and taenite (nickel-iron rich in nickel) known as plessite, (*b*) plessite is found alone, (*c*) plessite and taenite both occur. (3) Group above the lacuna. This contains the alloys rich in nickel, so-called taenite. Assuming the existence of a compound containing 68 per cent. of nickel, this group may be further subdivided according as the alloy contains more or less nickel than is required to form the compound. (4) Dystektite group. This consists of a definite chemical compound, assumed to be Ni_2Fe, and is held by Rinne to be represented by awaruite. It should be noted, however, that the work on this substance referred to above renders the existence of a definite compound somewhat doubtful. In concluding his paper, Rinne calls attention to the wide field of research presented by meteorites when studied from this point of view, and expresses his belief that the knowledge we already possess as to the influence of carbon, phosphorus, and sulphur in modifying the structure and properties of iron will afford the clue to the part played by cohenite, schreibersite, and troilite in the constitution of meteorites. Evidence that differentiation has really taken place after solidification is found in the fact that in some meteoric irons the relation of the kamacite to the troilite is such as to leave no doubt that the former crystallised after the latter had become solid. As troilite melts at 900°, this observation shows that the crystallisation of kamacite can take place at a temperature far below the melting point of the alloy.

Among the individual meteorites examined, the following may be noticed:

The Billings Meteorite.—This iron was found in southern Missouri and has been described by H. A. Ward,[1] and analysed by H. W. Nichols.

Cañon Diablo.—The investigation by Moissan[2] of the residue obtained on dissolving 53 kilograms of this iron in hydrochloric acid has already been referred to. It is interesting to notice that the crater of Coon Mountain, Arizona, twelve miles south-east of Cañon Diablo station, is believed by D. M. Barringer and B. C. Tilghman to have been produced by the impact of an immense meteorite of which the specimens of Cañon Diablo iron once formed a part.

Barraba, Cowra, and Mount Dyrring.—Careful analyses of these Australian meteorites have been published in full detail by J. C. H. Mingaye.[3] The first contains 93·50 per cent. of iron and 5·54 per cent. of nickel. The second consists mainly of 85·26 per cent. of

[1] *Amer. J. Sci.*, 1905, [iv], **19**, 240.
[2] *Ann. Chim. Phys.*, 1905, [viii], **5**, 174.
[3] *Rec. Geol. Surv., N.S. Wales*, 1904, **7**, 305.

iron and 13·23 per cent. of nickel. That of Mount Dyrring is of pallasite type, but much rusted.

Hvittis.—A. Lacroix [1] has called attention to the similarity in composition of this meteorite with that of Pillistfer. Both contain enstatite but no olivine.

Rodeo.—This iron has been shown by O. C. Farrington [2] to be an octahedrite of medium coarseness. It contains large inclusions of schreibersite and some graphite, but no troilite.

Shelburne.—This meteorite, which fell near the village of Shelburne, Grey Co., Ontario, in 1904, has been examined by L. H. Borgström,[3] who finds it to be a chondritic stone consisting mainly of olivine and enstatite.

Mount Vernon.—W. Tassin [4] has determined this to be a pallasite of the Krasnojarsk type. It consists essentially of nickel-iron containing olivine and varying amounts of troilite. The nickel-iron alloy, the taenite, schreibersite, troilite, chromite, and olivine were separated and their composition ascertained.

A. Hutchinson.

[1] *Bull. Soc. franç. Min.*, 1905, **28**, 70.
[2] *Field Columb. Mus.*, Pub. 101, 1905, **3**, 1.
[3] *Trans. R. Astronom. Soc. Canada*, 1905 (for 1904), 69.
[4] *Proc. United States Nat. Mus.*, 1905, **28**, 213.

RADIOACTIVITY.

VALUABLE and interesting advances have been made in this subject during the year, both from the theoretical and the experimental side. On the theoretical side no important modification has been made in the theory of atomic disintegration outlined in the last Report. This hypothesis continues to account satisfactorily for the experimental knowledge, and there is a growing tendency to interpret it even more literally and to pursue it more strictly to its logical conclusions from the chemical side. The adequate application of the idea of disintegration to other sciences, and in particular to cosmical physics, remains almost virgin territory, although numerous isolated phenomena of the widest diversity of character are being recognised as probable results of such a universal process.

The problems which have occupied the front rank in the year's work are undoubtedly those connected with the α-radiation, and definite advances are to be recorded in our knowledge of the ejection of the α-particle from the parent atom, of its chemical identity, and of the processes accompanying its passage through matter. The line of work originated by Bragg and Kleeman[1] has been extended and completed,[2] and their methods have been developed into a most powerful engine of research. The authors have analysed the α-radiation of radium into four distinct types or groups of different range or penetrative power, and they have assigned each type to a definite disintegration in the series. In this work only the first rapid changes of radium affect the results, as the later changes are too slow in period to have as yet been studied. (The expression "radioactive equilibrium of radium" in this and many similar connections refers to the equilibrium of the first rapidly changing products.) The range of each of the four types of α-rays from radium has been determined to an accuracy of 0·05 cm. in air. By "range" is to be understood the distance each α-particle travels after leaving the parent atom before it loses its ionising power and passes beyond the means of detection. A result indicated in the earlier work,

[1] *Ann. Reports*, 1904, 255 and 269.
[2] *Phil. Mag.*, 1905, [vi], **10**, 318 and 600.

but not included in the last Report, has been now definitely established. It is found that the ionising power, defined as the number of ions produced per unit length of path, *increases* with increasing length of path, and then ceases quite abruptly when at its maximum. The α-particles expelled from the radium atom itself in its change into the emanation have a range of 3·50 cm. and constitute the least penetrating type of the four. Those from radium C in its change into radium D are the most penetrating and have a range of 7·06 cm. Two intermediate types of range, 4·23 cm. and 4·83 cm. respectively, correspond to the two changes of the emanation into radium A and of the latter into radium B, but it has not yet been found possible to say which of the two types corresponds to each change.

It was definitely proved from the curves obtained that all the α-particles expelled in any one change have exactly the same range, and therefore, as the results to be considered show, the same initial velocity of expulsion. Moreover, when the radium preparation is in radioactive equilibrium the number of particles belonging to each type is the same, and the nature of the α-particles in the different types is identical in every respect save initial velocity of expulsion. This striking result is clearly proved in a graphical manner from the experimental curves; it has long been considered probable by Rutherford, from his earlier work on the nature of the α-radiation, and from the requirement of the simplest expression of the disintegration theory. If we suppose that only one α-particle is expelled from each atom in any change accompanied by α-radiation, it follows that the number of α-particles expelled in the successive disintegrations must be the same for each when the state of radioactive equilibrium is reached. This result, that all the α-particles expelled in each change are all alike among themselves, and that the different types expelled in different changes differ only in initial velocity of ejection, shows that Dalton's conception of the atom applies strictly to radioactive change. No difference of properties has ever been recognised between atoms of the same type; and when atoms disintegrate the lighter fragment is expelled with a definite measurable velocity, which is the same for all the atoms of the one type and different for atoms of different types. The speculations which have been advanced to account for the cause of disintegration, by attributing it to a gradual loss of the internal energy of the atom by radiation until a point of instability is reached, are on the other hand directly opposed to the Daltonian conception of the atom which the experience of chemistry and spectroscopy so strongly supports. It is satisfactory to note that the clear view of the disintegration process obtained from Bragg's work unequivocally supports the older view. The idea of a gradual change of the nature of atom with time derives no experimental support from radioactivity.

Bragg and Kleeman extended their researches to the passage of the α-particle through other substances than air. They deduced an important new general law, that the loss of range suffered by an α-particle in its passage through an atom was approximately proportional to the square-root of the atomic weight. Mixtures and compounds behave similarly. In either case the loss of range is proportional to the sum of the square-roots of the atomic weights of the constituent atoms. The law applies, so far as can be deduced, equally for each of the four types of α-particles expelled from radium, and therefore may be considered to apply generally to the α-radiation. The earlier researches on the absorption of the α-rays by matter, in which the existence of several distinct types in the α-radiation of one element was not recognised, are unreliable. There is no exponential law of absorption and no "density law" for the α-radiation. "Each α-particle pursues a rectilinear course, no matter what it encounters; it passes through all the atoms it meets, whether they form part of a solid or a gas (or in all probability of a liquid), suffering no deflection on account of any encounter until at any rate very near the end of its course. It loses energy as it goes, a portion of this at least being spent in producing ions. . . . A thin metal plate may be placed in the way of the stream, and so rob every particle of some of its energy, but not a single one is brought to rest by collision with the atoms of the metal, and the number of particles in the stream remains unchanged." This clear picture of the collision between a radiant atom and a stationary atom is fully justified by a consideration of the curves.

The square-root law was substantiated for silver, platinum, gold, tin, copper, aluminium, lead, iron, and nickel among the metals, and for methyl bromide, methyl iodide, ethyl chloride, ethyl iodide, carbon tetrachloride, chloroform, pentane, benzene, carbon disulphide, carbon dioxide, oxygen, and hydrogen among the gases. The law is approximate, but ether is slightly irregular, and in addition there is a small but distinct difference of stopping power between the metals and gases. If the stopping power is plotted against the square-root of the atomic weight (or the sum of the square-roots of the constituent atomic weights), the two classes of substances fall on straight lines inclined to each other at a slight angle, the complex gas molecules appearing to possess rather greater stopping power than the metals.

The results put into the hands of chemists a novel method for the determination of atomic weights, although the experimental difficulties are at present very great. Such a method should prove invaluable for the monatomic gases, for which the evidence of atomic weight is confined solely to density determinations. In view of the discrepancy between the accepted atomic weight of helium and Rutherford's determination of the mass of the α-particle, additional evidence of the atomic weight

of this element would be very welcome at the present time, and it is to be hoped that the observers will be able to extend their results to include the monatomic gases.

In a later paper, Bragg[1] deals with the question whether the number of ions produced by the α-ray in different gases is the same. In the simple ionisation theory for voltages above the saturating voltage the current should be independent of the voltage, and it is well known that this law is only approximate. With the complex gases the deviations are much exaggerated, and Bragg attributes them to a new kind of recombination between the ions, not allowed for in the simple theory. This special kind he terms "initial recombination," to distinguish it from general recombination. The initial recombination he attributes to the reunion of the newly formed pair of ions, which is proportional to the number of ions produced, whereas general recombination is proportional to the square of the number present. The latter effect can be reduced at will by making the ionisation very feeble. In such a particular case it was shown that only 1/3000th of the total number of ions produced was lost by general recombination, while the current with 25 volts was only 80 per cent. of the current with 1000 volts. In ethyl chloride under 60 cm. pressure, 2000 to 3000 volts were necessary to secure saturation, but when the latter condition was secured the total number of ions produced in ethyl chloride by the passage of an α-particle was considerably greater than in air, although in the first experiments under ordinary conditions it appeared less. The general explanation of the effect seems to be bound up with the fact that the act of ionisation is essentially an atomic and not a molecular process. In a complex molecule each atom has several very near neighbours, which may attract and recombine with an electron displaced from another atom in the same molecule before the electron moves beyond the sphere of attraction of its parent atom. If more than one atom in the complex molecule loses an electron, the electric field in its neighbourhood is more intense, and the chance of the ejected electron returning to the system is the greater.

Independently of the above results, Rutherford has continued his researches on the nature of the α-ray. The intimate connection between the conclusions drawn by the two authors independently form a feature of the year's work. A new series of determinations of the velocity and of the ratio e/m of the charge to the mass of the α-particles expelled from radium closely confirmed the earlier measurements.[2] Use was made of the discovery of Bragg that the α-particles expelled in any one disintegration all possess the same range, and therefore presumably travel at the same velocity, to give definiteness to the measurement of

[1] *Trans. Roy. Soc. S. Australia*, 1905, **29**, 187.
[2] *Phil. Mag.*, 1905, [vi], **10**, 163.

the velocity. Before, only the average velocity of the four groups was determined. In the present research, the measurements were made on a single type of homogeneous α-particles. The α-particles expelled from radium C were selected as the standard, for besides being the most penetrating they can be obtained homogeneous and under conditions where no absorption occurs in the active matter itself. A platinum wire was exposed to the action of the emanation and kept negatively charged to concentrate the excited activity on it. The rays from radium A decay practically to zero fifteen minutes after the removal of the wire from the emanation, and since radium B gives out no rays, from that time the α-radiation is homogeneous, comprising only the α-particles expelled from radium C. The actual mass of the active deposit is so insignificant that the real initial velocity of projection is obtained undiminished by absorption in passing through the material. The deflection of the rays was determined by Becquerel's photographic method in a partial vacuum. The value found for mv/e was $3{\cdot}98 \times 10^5$. The experiments on the electrostatic deviation are not complete. From other determinations of the heating effect or kinetic energy of the α-particles, and of the number of α-particles produced per gram of radium per second, it was calculated that $v = 2{\cdot}6 \times 10^9$ cm. per second, and $e/m = 6{\cdot}5 \times 10^3$ E.M. units. These results are practically identical with the earlier ones, but the author does not consider that sufficient weight can be attached to them to bear on the important question of the nature of the α-particle. The atomic weight of the α-particle calculated from the data is 1·51 (H = 1).

Another new determination of the magnetic and electrostatic deviation of the α-rays of radium has been carried out by A. Stanley Mackenzie.[1] The position of the deflected beam was determined by the phosphorescence of a zinc sulphide screen recorded photographically, and the whole complex beam was used. The mean value for mv/e was $3{\cdot}0 \times 10^5$, the extremes being $2{\cdot}5 \times 10^5$ and $3{\cdot}7 \times 10^5$, but the rays had to pass through a thickness of mica estimated to decrease the initial velocity by 6 per cent. The results of the electrostatic deviation gave $v = 1{\cdot}18 \times 10^9$, $1{\cdot}45 \times 10^9$, and $1{\cdot}74 \times 10^9$ cm. per second for the slowest, mean, and fastest particles respectively, whilst the value of e/m was $4{\cdot}6 \times 10^3$. For the α-particle of polonium the value of mv/e was $3{\cdot}3 \times 10^5$. It is doubtful whether these results can be given more weight than the earlier ones of Rutherford and Des Coudres in the discussion of the nature of the α-particle.

Rutherford[2] passed the radiation from radium C through successive thicknesses of aluminium foil, and determined the magnetic deviation after each penetration. A clear photographic effect could be obtained through 12 layers of thickness 0·00031 cm., but no effect at all

[1] *Phil. Mag.*, 1905, [vi], **10**, 538. [2] *Loc. cit.*

through 13 layers. The photographic effect ceases abruptly after passage through a thickness of aluminium greater than 0·0037 and less than 0·0040 cm. It was found that the velocity of the α-particle regularly decreased with each successive penetration of a thickness of foil. The velocity of the particle, as determined from the magnetic deviation, after passage through 0·0037 cm. was found to be still 64 per cent. of the initial. So that the particles still possess 41 per cent. of their initial kinetic energy when they cease to affect the photographic plate. It was shown that each layer of foil had the same effect in stopping the α-particles as 0·54 cm. of air, so that 12 layers would correspond to 6·5 cm., and 13 to 7 cm. of air. This showed that the α-particles ceased to produce a photographic effect at the same velocity as that at which Bragg showed they cease to ionise. In addition it was proved that the phosphorescent action of the α-rays of radium C ceased after passage through 6·5 cm. of air, or 12 thicknesses of aluminium foil. The α-particle of radium ceases to produce either photographic, fluorescent, or ionising action at the same speed, and in the case of radium C this speed is still over 60 per cent. of the initial speed of expulsion, or $1{\cdot}3 \times 10^9$ cm. per second. This is a most remarkable and important result, and in the author's view indicates clearly that all three phenomena have a common cause, and that the photographic and fluorescent action are both primarily caused by ionisation. Rutherford shows from his results, and the value of the ranges in air given by Bragg, that the velocity of the other particles of radium can be calculated in terms of that of radium C. Expressing the latter by V, and using for the calculation the more recent determinations of Bragg, we have—from radium 0·87 V, from the emanation 0·89 V or 0·91 V, and from radium A 0·91 V or 0·89 V. The mean velocity is 0·92 V, and the different α-particles do not differ in velocity more than 8 per cent. from the mean value. In conclusion, Rutherford points out that if in any atomic disintegration an α-particle were expelled with a velocity below $1{\cdot}5 \times 10^9$ cm. per second it would be beyond the means of detection and the change would be a rayless one, so that ordinary matter may be undergoing comparatively rapid transformation without producing appreciable effects.

The view that the photographic action and also the view that the fluorescent action of radiations is primarily an ionising action have been brought forward independently during the year. J. Joly[1] from general photographic evidence concluded that photographic action is due to ionisation. The main arguments used were—(1) the connection between photographically active and photoelectric substances, both the haloid salts of silver and the organic dyes used to produce colour-sensitiveness being strongly photoelectric ; (2) the persistence of photographic effect

[1] *Nature*, 1905, **72**, 308.

at low temperature, proving that the action must be atomic and not molecular (Dewar), and the fact that photoelectric action also persists at low temperature; (3) the common ionising and photographic action of such a variety of different types of radiation; (4) the possibility of explaining photographic reversals on this view. In the latent image there may be a rising potential between the groups of ions until ultimately a point is reached where there is a spontaneous discharge and neutralisation causing photographic reversal.

G. T. Beilby [1] investigated the fluorescence of barium platinocyanide under the action of the β- and γ-rays of radium. He showed that the loss of fluorescent power or fatigue of the crystals after prolonged fluorescence was due to a change from the crystalline to the amorphous state analogous to that produced by mechanical flow in his experiments on metals. After prolonged action of the rays, the fluorescent power of the crystals fell to about 8 per cent. of the initial and did not further diminish. The crystals are reddened and the change is permanent, neither the original colour nor the fluorescence being recovered by keeping either in the dark or in the light. Exactly the same effect on the colour and fluorescence power is produced by causing the crystals to flow mechanically with an agate pestle, and both the fatigued and the flowed specimens recover their original properties partially by heating and completely by solution and recrystallising. The second part of the paper deals with the secondary phosphorescence exhibited by certain substances after removal from the action of the rays, and with the phenomenon of thermoluminescence or revived phosphorescence induced in a substance previously exposed to radium by the action of heat. He shows that the various actions can be explained on the view that the rays ionise the substance, and that the ions remain insulated and stored up in the substance under some conditions for considerable periods, the insulation being broken down on heating.

Referring to the important result of Rutherford that the α-particle still possesses 60 per cent. of its original velocity when it ceases to ionise, Bragg [2] deduces from his results that this critical velocity must be exactly the same in all gases, otherwise the curves obtained in dealing with a mixture of gases should consist of the several simple curves overlapping; but no trace of such an effect exists. This strengthens the argument that the act of ionisation must be the same for all gases. A further conclusion is drawn as to the relation between the velocity of the α-particle and its ionising power for unit-length of path. It is deduced that the ionising power is proportional to the square-root of the speed, a result which is to be expected if the force acting between the radiant atom and the atom with which it collides is a function of their mutual distance.

[1] *Proc. Roy. Soc.*, 1905, **74**, 506. [2] *Phil. Mag.*, 1905, [vi], 600.

These conclusions of Rutherford and Bragg with regard to the nature of the α-ray have been criticised by Becquerel,[1] who maintains his earlier results that the α-rays behave as a homogeneous beam, all the particles possessing the same deviability in the magnetic field, and that the radius of curvature increases with the length of the path, instead of decreasing as Rutherford finds. To account for this increase, Becquerel has put forward the view that the value of the mass to the charge increases with the length of path owing to the mass being augmented by the particle attracting other particles to it. The replies of Rutherford and Bragg to this criticism are to be found in the current numbers of the *Philosophical Magazine* and *Physikalische Zeitschrift* respectively. The controversy is extremely interesting, but is too highly technical to be dealt with profitably without diagrams.

McClelland[2] has found that a relation holds between the atomic weight of a metal and the secondary radiation to which it gives rise when struck by the β-rays of radium. The secondary radiation is the greater the greater the atomic weight, but is not proportional to it, and increases less rapidly than the atomic weight.

The elements fall into well-defined divisions when the atomic weight is plotted against the secondary radiation, and these divisions correspond exactly to the division into periods of the periodic table. A broken curve is obtained, the increase of secondary radiation with the atomic weight being greatest for the electropositive and least for the electronegative elements, whilst in the change from one period to the next there is very little increase in the secondary radiation. The results tend to confirm the view of J. J. Thomson as to the electronic constitution of matter. They add another interesting example to the general periodicity of physical as well as chemical properties first elucidated by Lothar Meyer.

The important questions[3] connected with the positive charge carried by the α-particle have been the subject of much work during the year, but no final conclusion is yet possible. J. J. Thomson[4] showed that radium and polonium in a good vacuum emit besides α-particles a copious stream of slow-moving electrons, which in ordinary circumstances neutralise the positive charge carried by the α-particles. If a magnetic field is applied, the electrons can be disentangled from the α-particles, and the latter then conveyed a positive charge to a plate on which they impinged. Rutherford,[5] using the same means for eliminating the slow-moving electrons, succeeded in measuring the total positive charge conveyed by the α-rays from a known weight of radium. If the α-particles are assumed to carry the atomic charge, that is, are

[1] *Compt. rend.*, 1905, **141**, 485.
[2] *Trans. Roy. Dub. Soc.*, 1905, **19**, [ii], 1.
[3] *Ann. Reports*, 1904, 255.
[4] *Proc. Cam. Phil. Soc.*, 1905, **13**, 49.
[5] *Phil. Mag.*, 1905, [vi], **10**, 193.

minus one electron, it was deduced that 1 gram of radium (element) must expel $6{\cdot}2 \times 10^{10}$ α-particles per second for each change it undergoes, or $2{\cdot}5 \times 10^{11}$ α-particles in the first four rapid changes. Rutherford concluded that there was no obvious reason for supposing that the α-particles are not charged at the moment of their expulsion. The total number of β-particles expelled per gram of radium in radioactive equilibrium per second was $7{\cdot}3 \times 10^{10}$, confirming in a most interesting manner the result indicated by theory that four α-particles are expelled to each β-particle. From the number of atoms disintegrating per second, Rutherford deduces that λ for radium is $5{\cdot}4 \times 10^{-4}$ (year)$^{-1}$, the time for half-transformation 1280 years, and the average life of the radium atom 1850 years, which is in good accordance with previous estimates.

J. J. Thomson [1] announced that uranium as well as radium and polonium emit the slow-moving electrons, and the writer [2] suggested that these electrons might be derived from the α-particles themselves, which are expelled initially unchanged, but lose electrons on collision with the gas molecules, so that the negative charge carried by these electrons exactly neutralises the positive charge carried by the α-particles. Miss Slater [3] has shown that the emanations of both radium and thorium give out the slow-moving electrons as well as α-rays in their change into radium A and thorium A, so that it appears that the effect is general for the expulsion of the α-ray. It is clear from Bragg's curves that the α-particles from the thinnest so-called "film" of radium salt have on the average passed through many molecules of the salt. The experimental results so far recorded are to be expected on either view, and the question whether the α-particle is charged initially after expulsion has not been settled.

In connection with the nature of the α-particle there can be little doubt that it consists of an atom of helium. Debierne has shown that helium is produced from actinium to an extent comparable to its rate of production from radium of equal activity. First working with 100 milligrams of radium bromide in a manner similar to that employed by Ramsay and Soddy, he found that with practice he could repeat their results in a very regular manner, and obtained tubes showing an intense spectrum of helium. The solution did not appear to become exhausted, but the production took place regularly. Working with actinium, both in solution and in the state of fluoride free from water, Debierne found in each case a production of helium comparable to the activity of the preparation. Himstedt and Meyer [4] have given the result of further experiments, mostly blank tests, on the production of helium from radium. The writer has attempted to measure accurately the amount of helium produced from uranium and thorium, and in one

[1] *Nature*, 1905, **71**, 438.
[2] *Ibid.*
[3] *Phil. Mag.*, 1905, [vi], **10**, 460.
[4] *Ann. Physik.*, 1905, [iv], **17**, 1005.

experiment—the only successful one so far obtained—got from uranium indications of helium in about the quantity to be expected from the theory that the α-particle is an atom of helium.[1] The only successful experiment with thorium was of the nature of a blank test, and proved that the rate of production was not greater than ten times that to be expected from theory. It is hoped, as the experimental difficulties in the detection of these infinitesimal quantities of helium have been overcome, the results will give in due course a definite answer to the question of the nature of the α-particle.

In the department of radioactive change, advances have been made in our knowledge of the disintegration series of each of the elements, uranium, thorium, radium, and actinium. One of the most important is the successful separation of a new radioactive constituent possessing thorium radioactivity from the Ceylon mineral thorianite, by Ramsay and Hahn. Thorianite has been shown by Dunstan and Blake[2] to consist of about 70 per cent. of thorium in the form of dioxide soluble in nitric acid. It possesses an activity comparable to that of the pitchblende from Joachimsthal, and contains several times as much helium as any mineral known. Ramsay worked up 250 kilograms for radium, and the carbonates of the alkaline earth group obtained from it weighed 18 grams and possessed an activity about 500 (uranium = 1). This was submitted to fractionation by Giesel's process,[3] but it was found that the activity concentrated both in the more soluble and in the less soluble portions, the middle fractions being the least active. Ultimately it was proved that a small part only of the activity was due to radium, the major part being due to a new type of matter named appropriately "radiothorium" and possessing thorium radioactivity to a very intense degree. Weight for weight, the new product was shown to be at least 100,000 times as active as thorium. The activity was accurately determined by the relative amount of thorium emanation evolved from the two substances, and for one preparation an activity of 690,000 is recorded. The identity of the activity of radiothorium with that of thorium was shown by a comparison of the constant of decay of the emanation and excited activity from the two substances, and also by the fact that radiothorium produces thorium X exactly as in the case of thorium.

The results indicate that there is an intermediate substance, radiothorium, between thorium and thorium X, with a chemical nature extremely closely allied to thorium. Two questions arise. Since the radioactivity of radiothorium is comparable to radium, the period of average life must also be of the same order for each, or about a thousand

[1] *Nature*, 1905, **73**, 151.
[2] *Proc. Roy. Soc.*, 1905, **76**, Series *B*, 253.
[3] Hahn, *Jahrb. Radioakt. Elektronik*, 1905, [ii], 233.

years. As the average life is short, radiothorium must possess a parent element in thorianite, and the question arises as to whether thorium is the parent. If thorium is the parent, it would seem that the original change of thorium into radiothorium is probably "rayless," so that pure thorium would be inactive, and the "non-separable activity" due to radiothorium. This would account at once for the apparent constancy of activity of thorium preparations, and for the existence of inactive thorium repeatedly affirmed by Hofmann and Zerban. This view, although rendered almost necessary by the results in Hahn's paper, has not yet been definitely established. No measurements are given in the paper of the activity of the thorium obtained from the thorianite to see if this is less than usual, and it has not been found possible to separate radiothorium from ordinary radioactive thorium.

Sackur [1] attempted to separate from thorium a radioactive constituent, but failed to obtain a constantly active substance, or to effect a lasting concentration of the radioactivity.

Elster and Geitel [2] obtained from the spring at Baden-Baden a precipitate which gave considerably more thorium emanation than a similar weight of thorium. Giesel [3] obtained from the residues from monazite sand, after removal of thorium, preparations which possessed thorium radioactivity ten times as great as ordinary thorium. Presumably this activity was permanent, and, if so, must have been due to radiothorium, not merely to thorium X. Baskerville and Zerban [4] describe a new source of inactive thorium, a rock obtained from South America, consisting mainly of barium carbonate with a very small percentage of thorium. As in previous communications on inactive thorium, the statement is made that no radiations are given off, but no details as to the method of testing are given. Such measurements as are given are merely photographic tests. It may be mentioned here that Baskerville's work on the separation of two new elements, carolinum and berzelium, from ordinary thorium is, as the author himself points out, purely chemical work, and does not bear directly on the question of the radioactivity of thorium. Zerban,[5] in support of the view previously expressed by Hofmann and himself that active thorium is only obtained from minerals containing uranium, and when the latter element is absent the thorium obtained from the mineral is inactive, announced that he had detected 0·02 per cent. of uranium in crystallised Norwegian monazite, and that the composition of this mineral does not oppose the view. If Hofmann and Zerban's supposition is correct, it would appear to indicate that uranium rather than thorium was the parent of radiothorium, and that

[1] *Ber.*, 1905, **38**, 1756.
[2] *Phys. Zeit.*, 1905, **6**, 67.
[3] *Ber.*, 1905, **38**, 2334.
[4] *Chem. News*, 1905, **91**, 74.
[5] *Ber.*, 1905, **38**, 557.

the latter's association with thorium was not generic but due to its great similarity of chemical nature.

Miss Slater [1] has shown that the periods of thorium A and thorium B must be transposed. Thorium A changes into thorium B without emitting rays, but the time for half-transformation is eleven hours, whilst the period of fifty-five minutes belongs to the α- and β-ray change of thorium B into the unknown inactive end-product.

A careful examination of the conditions under which thorium X may be separated from thorium has been carried out by Schlundt and Moore.[2] They find the action of pyridine and fumaric acid similar to that of ammonia, in that all three reagents precipitate thorium and leave thorium X in solution. Pyridine leaves more thorium A in solution than ammonia, and thorium A may be obtained pure by precipitating first with ammonia, then redissolving the precipitate, and reprecipitating the thorium with pyridine. Fumaric acid, on the other hand, leaves all the thorium A in the solution and precipitates thorium B only with the thorium. The latter, therefore, after the lapse of five hours during which the thorium B changes completely, gives the 25 per cent. non-separable activity due to the first α-ray change. They confirmed Miss Slater's result of the relative period of thorium A and thorium B, and separated pure thorium B by electrolysis. A large number of organic reagents were found to precipitate thorium, leaving a part of the active matter in solution. Thorium fumarate is stated to possess the highest emanating power known of any thorium compound in the solid state. Inactive thorium was never obtained. F. v. Lerch,[3] continuing his work on the electrolysis of thorium solutions and the separation of the active products, shows that electrolysis and the action of metals precipitate only the matter causing the excited activity (thorium A and thorium B) and no thorium X from acid solutions, but in alkaline solutions thorium X is precipitated. These results were obtained by a careful examination of the rate of decay of the activity of the preparations.

In the disintegration series of radium there is much new matter to be included. The diagram given in the last Report (p. 268) must be supplemented by the addition of another stage between radium D and radium E.[4] In consequence, what was before named radium E (polonium, radiotellurium) must be termed radium F. The period of half-transformation before given for radium D (forty years) remains unchanged, but this is a rayless change. The β-ray results in the change of radium E into radium F, and the half-period for this

[1] *Phil. Mag.*, 1905, [vi], **9**, 628.
[2] *J. Phys. Chem.*, 1905, **9**, 682.
[3] *Wien. Sitzungsber.*, 1905, **114**, [iia], 1.
[4] Rutherford, *Phil. Mag.*, 1905, [vi], **10**, 290.

substance is six days. In addition it will be convenient to include here a recent paper of Bronson [1] which shows that the periods of radium B and radium C must be transposed and decreased, the correct rate for radium B being twenty-six minutes and of radium C twenty-one minutes (for half-transformation). Rutherford has incorporated all these results with the exception of the last (Bronson) in a new edition of his book,[2] and has dealt very fully with the experimental evidence and the theory in these succeeding changes. He points out that when a rayless change is followed by a change in which rays are expelled, the decay curves of the radiation reveal the constants of both changes but do not indicate which constant applies to each change. This can be determined only after a chemical separation of the products. Miss Slater separated thorium A from thorium B by volatilisation, the latter being more readily volatilised by heat than the former, whereas by the bombardment of the substance by cathode rays *in vacuo* the opposite obtains. The earlier results of v. Lerch and of Pegram obtained in the electrolysis of thorium solutions are in full agreement with the latest results. Bronson showed that radium B is more readily volatilised by heat than radium C, and succeeded in separating the latter and measuring its decay constant alone.

With reference to actinium, Godlewski [3] succeeded in separating from this substance a product, actinium X, in every way analogous to thorium X and intermediate between the parent element and the emanation. The method employed was identical with that employed by Rutherford and Soddy for thorium X. The period of half-transformation was found to be 10·2 days. Unlike the case of thorium, the removal of actinium X reduces the activity of the parent element to only 5 per cent. of the initial value, so that it is indicated that the initial change of actinium into actinium X is a rayless change.

Giesel [4] and Marckwald [5] have both independently brought forward evidence agreeing with the above on the existence of actinium X.

Hahn and Sackur have established the identity of the actinium of Debierne and the emanium of Giesel [6] by showing that the constants of decay of the emanation and excited activity are the same for both substances. They obtained for the periods of half-transformation 3·6 seconds and 3·9 seconds for the emanation of actinium and emanium respectively, and 36·5 minutes for the excited activity in each case.

Godlewski [7] has shown that the β-rays of actinium are peculiar in that they are homogeneous, and are absorbed by matter according to a

[1] *Phil. Mag.*, 1906, [vi], **11**, 143.
[2] *Radioactivity*, Camb. Univ. Press, 1905.
[3] *Phil. Mag.*, 1905, [vi], **10**, 35.
[4] *Ber.*, 1905, **38**, 775.
[5] *Ibid.*, 2264.
[6] *Ibid.*, 1943.
[7] *Phil. Mag.*, 1905, [vi], **10**, 44.

strictly exponential law. They are moreover of only half the penetrating power of the β-rays of any other element, whilst the γ-rays of actinium are only one-quarter as penetrating as those of radium. The resemblance between actinium and thorium in their respective disintegration is almost complete, both in the number and nature of the changes. Bronson has pointed out that in all three elements, radium, actinium, and thorium, the rayless change is of a longer period than the one immediately following. This is true for both rayless changes of radium. In all four cases the change next following the rayless change is accompanied by the expulsion of a β-ray. The general resemblance in character and relative period of the succeeding members of the various disintegration series on the one hand, and their distinct individual peculiarities on the other, are most fascinating and mysterious. We seem to have here an extension of similar relations expressed for elementary matter generally by the periodic law, and there is no doubt that any explanation of the one will have an application to the other.

Godlewski [1] has satisfactorily explained some anomalies in the rate of decay of uranium X obtained by Meyer and von Schweidler [2] by showing that the uranium X was unequally distributed in the salts prepared in their experiments, and that the gradual equalisation of the concentration of the uranium X by diffusion through the mass accounts satisfactorily for the anomalies observed.

Becquerel has shown that uranium X can be removed from uranium solutions by boiling with lampblack, as the latter withdraws the uranium X from the solution.[3]

The production of radium from uranium has now been definitely established by direct experiment and also by indirect methods. The writer [4] freed a kilogram of uranium nitrate from radium by successive precipitations in its solution of barium sulphate, and showed by means of the emanation test that the amount of radium 567 days after purification was more than a hundred times greater than at first. The rate of growth was estimated to be only of the order of one-thousandth part of that to be expected from the theory on the assumption that uranium X changes directly into radium. From this and other evidence to be given later, it is extremely probable that several intermediate forms exist between uranium X and radium, with long periods of transformation, causing the initial rate to be diminished.

Boltwood [5] has criticised this result. Working with 100 grams of uranium nitrate, purified originally from radium by repeated crystallisation from water, he obtained no detectable increase in the

[1] *Phil. Mag.*, 1905, [vi], **10**, 45.
[2] *Wien. Sitzungsber.*, 1904, **113**, [iia], 1057.
[3] *Compt. rend.*, 1905, **141**, 485.
[4] *Phil. Mag.*, 1905, [vi], **9**, 768.
[5] *Amer. J. Sci.*, 1905, **20**, 239.

amount of emanation produced after a period of 390 days, and concludes that the results obtained by the writer are "without significance." Boltwood's experimental results are, however, in complete agreement with the writer's experience, for with so small a quantity for so short a time the effect would not be within the means of detection. The criticism appears to be based on a false comparison between the two experiments. The experiments are not comparable, and the relation between them need not here be further discussed.

McCoy [1] first showed that the radioactivity of the uranium minerals not containing thorium is proportional to the quantity of uranium present, which is indirect evidence that uranium is the parent of the other radio-elements, radium and actinium, present in the mineral. Strutt [2] and Boltwood [3] have investigated the ratio between the uranium and radium in the various uranium minerals. Boltwood obtained results for twenty-one minerals showing that in all cases the ratio between the two elements is surprisingly constant and that the "inevitable and only possible conclusion is that uranium is the parent element of radium." He determined the amount of uranium by analysis, and the radium from the amount of emanation released on dissolving the mineral and the amount released spontaneously by the mineral in the solid state. Strutt used a more direct method of estimating the radium in that the solution of the mineral was allowed to accumulate emanation for a definite time. His results for 20 minerals showed much greater variations in the ratio than in the former case, but the approximate proportionality was clearly brought out. Strutt pointed out that thorium seemed to be inevitably accompanied by the uranium-radium series, although minerals containing the latter in which thorium is absent are common. The minerals richest in helium are richest in thorium although the converse does not hold.

Marckwald has continued his work on radiotellurium or polonium,[4] and finds that this element comports itself chemically in every respect as the missing element of the sulphur-selenium-tellurium family. It thus bears the same relation to tellurium as radium bears to barium. Fifteen tons of pitchblende yielded 5 tons of residues after the extraction of the uranium, and from this material 16 grams of selenium, tellurium, and radiotellurium were precipitated by sulphur dioxide. The gradation of properties from selenium to radiotellurium is shown in the action of their oxides towards ammonia. Tellurium, although giving an oxide possessing acidic properties and dissolving in ammonia, does not form a stable compound. The oxide of radiotellurium is not dissolved by ammonia. The residue from the 16 grams after treatment with ammonia weighed 3 milligrams and contained all the active matter.

[1] *Ber.*, 1904, **37**, 2641.
[2] *Proc. Roy. Soc.*, 1905, **76**, Series *A*, 88.
[3] *Phil. Mag.*, 1905, [vi], **9**, 599.
[4] *Ber.*, 1905, **38**, 591.

The vexed question as to the constancy or otherwise of the radiation from radiotellurium has been settled. Meyer and von Schweidler [1] have determined the decay constant and found it to be normal, the period of half-transformation being 135 days. Marckwald has confirmed this and obtained the value 139 days. Finally, Rutherford [2] compared the rate of decay of radiotellurium with radium F and obtained the same constant for each (143 days). He calculates from this the quantity of this substance in pitchblende containing 50 per cent. of uranium to be about a milligram in 7 tons, and the α-ray activity of pure radium F to be about 800 times that of radium in radioactive equilibrium. The constant proportion of radium in the uranium minerals he determined in conjunction with Boltwood to be 0·72 gram of radium per ton of uranium.[3] A knowledge of this constant obviates the necessity of estimating the radium-content of minerals if the uranium-content is known. The evidence with reference to the polonium of Mme. Curie, although acquired only after great labour and by the co-operation of many, is now far more striking than for the case of radium. Here we have a case of an ordinary chemical element, the position of which has been found in the periodic table, and the chemical nature of which is completely determined, changing so rapidly that only half survives after five months, and giving out in the process nearly a thousand times the energy which a similar weight of radium gives out in a similar time. To-day, with our theoretical knowledge, however, such an amazing result calls for no special treatment and hardly awakens surprise.

Since radium F has been shown by Marckwald to comport itself as the missing heavy sulphur element, its atomic weight must be the next higher to bismuth, and therefore between 210 and 212. This very strongly supports the view that the α-particle is an atom of helium, for in the change from radium into radium F four α-particles are expelled, and a reduction of about fifteen units is therefore to be expected. A further step is possible because radium F expels an α-particle in its change into the unknown radium G. Radium G is the apparent end of the series and is unknown because it is not changing, so that it is to be expected that radium G is likely to prove to be a well-known element. If the atomic weight of radium F is 210 to 212 the choice of the identity of radium G would appear to rest between bismuth and lead. Boltwood has called attention to the presence of lead in the uranium minerals and has suggested that it is one of the final products. The experimental verification of this may be confidently expected owing to the rapid period of change of radium F and the easy methods of separating it from the mineral worked out by Marckwald.

The results also have a bearing on the question of the production of

[1] *Wien. Sitzungsber.*, 1905, **114**, [iia], 5. [2] *Phil. Mag.*, 1905, [vi], **10**, 300.
[3] *Radioactivity*, 1905, 462.

uranium from radium. Here, as in the case of the change of uranium into radium F, a reduction of 13 units occurs, so that it is to be expected that three or four changes accompanied by α-radiation would occur in the transformation. Only one change is at present known, but the existence of intermediate products of slow period between uranium and radium already suggested is made more probable by these considerations.

Donald Murray has suggested[1] that the constant companionship of lead and silver in their ores indicates that silver is a disintegration product of lead, and the writer[2] from economic evidence has suggested that gold is a member of a disintegration series, and that its concentration in its ores is, as in the uranium-radium minerals, fixed on the average by the ratio between its rate of change and that of its parent element.

In conclusion, attention may be directed to a highly interesting and suggestive paper by J. J. Thomson[3] on the emission of electrons by the alkali metals. The paper breaks entirely new ground in that the author shows that the well-known phenomenon of the emission of electrons from metals exposed to the action of ultra-violet light, occurs also to a very small extent in absolute darkness in the case of rubidium and of the liquid alloy of sodium and potassium. An electroscope, sealed up in the flask which contained the alkali metal in a vacuum produced by Dewar's method, lost a positive charge even when kept in absolute darkness, although there was no perceptible leak when the leaf was negatively charged. It was also shown that sodium in the state of vapour gives out electrons the same as when in the solid state. In this experiment, light was not excluded. The sodium was vaporised in an exhausted glass flask, and in the vapour two oppositely charged wires were immersed. It was found that the sodium vapour tended to condense almost exclusively on the negatively charged electrode, in a manner exactly analogous to that in which the excited activity produced by the radioactive emanations is concentrated on the negative electrode.

If the emission of electrons from the alkali metals does take place spontaneously, and independently of the action of external influences, the phenomenon becomes in that respect allied to natural radioactivity. The author concludes therefore that it involves the explanation that the energy of the process is derived from the internal energy of the atom, or, in other words, the alkali metals no less than the radio-elements must be spontaneously undergoing atomic changes. The action of light in accelerating this process must be regarded as analogous to that of a detonator causing the atoms on which they impinge to explode, and the energy evolved in the process must be regarded as being derived

[1] *Nature*, 1905, **73**, 125. [2] *Ibid.*, 151.
[3] *Phil. Mag.*, 1905, [vi], **10**, 584.

from the internal energy of the atom rather than from the energy of the electric field in the light-wave. This view leads to the further conclusion that the tapping of the internal energy of the atom is to some extent under control and can in certain cases be effected by the action of light and other agencies.

These considerations are so opposed to the experience derived from the study of radioactive transformations that it may be considered very doubtful if the processes are analogous. It is certain that the mere loss or gain of an electron by an atom does not of itself constitute a change analogous to that suffered by the radio-elements. In the writer's opinion, the loss of electrons—produced, for example, in a piece of glass when it is rubbed on silk—should be distinguished from atomic disintegration in the sense it is employed in radioactivity, although sometimes, as in the disintegration of uranium X, radioactive change is accompanied by the expulsion of an electron alone. The loss of electrons by the alkali metals seems to be more nearly allied to the numerous ionic changes dealt with in chemistry—for example, the change of the ferrous into the ferric ion—and to possess the characteristics of the latter rather than to a disintegration like that of uranium X. The source of the energy on this view would be the ordinary chemical energy and not the internal energy of the atom.

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